Safe Deactivation of Energetic Materials and Use of By-products as Epoxy Curing Agents

Final Report – SERDP Project CP-1079

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Abstract

Sandia National Laboratories is developing innovative alternative technology to replace open burn/open detonation (OB/OD) operations for the destruction and disposal of obsolete, excess, and off-spec energetic materials. Alternatives to OB/OD are necessary to comply with increasingly stringent regulations. This program is developing an alternative technology to destruct energetic materials using organic amines with minimal discharge of toxic chemicals to the environment and defining the application of the by-products for the manufacture of structural materials.

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Sandia National Laboratories is developing innovative alternative technology to replace open burn/open detonation (OB/OD) operations for the destruction and disposal of obsolete, excess and off-spec energetic materials. Alternatives to OB/OD are necessary to comply with increasingly stringent regulations. This program is developing an alternative technology to destruct energetic materials using organic amines with minimal discharge of toxic chemicals to the environment and defining the application of the by-products for the manufacture of structural materials.

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Introduction

The DoD has a significant number of weapons components which need destroying. The Department of Defense (DoD) faces many environmental and legal issues in the demilitarization of these obsolete and excess energetic materials and assembled munitions. The current DoD stockpile of energetic materials that needs to be destroyed is about 700,000 tons. This total increases at a rate of approximately 60,000 tons per year.

Organic amines were found to react with TNT, RDX and Comp B at moderate temperatures, leading to a safe breakdown of the explosive materials without detonation, deflagration, or uncontrolled cook-off. The reaction of the explosive materials with the amines resulted in evolution of gaseous products, which were collected and analyzed. The resulting liquid by-products were found to be effective curing agents for conventional epoxy resins. Epoxies produced by this method were found to be safe and non-detonable. Mechanical properties of these epoxies were measured and can be tailored to the final requirements of any epoxy use. Commercial uses for this epoxy could complete the recycle of explosives.

Excerpts from the Joint Ordnance Commanders Group FY95 report[1] to Congress, summarizes the overview of munitions demilitarization. (A more current version will be published September 2001. This is the most recent report available at this time.) Looking to the future, the Army Science Board emphasizes including the life-cycle of the energetics in the early stages of designing and acquiring weapons. Table 1 lists the current stockpiles as of 31 March 1999. The generation of energetics forecasted for the period of FY2000 – 2009 is found in Table 2. Tables 1 and 2 list the amounts TNT and RDX found in the MIDAS[1] (www.dac.army.mil/TD/Midas) database.

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Table 1. Estimation of Current and Forecasted Conventional Ammunition Inventories   (31 March 1999)

Type of Explosive	Current (lbs)	Forecasted (lbs)	Total (lbs)
Composition A, 91%TNT	7,319,586	14,806,530	22,126,116
Composition B, 60%TNT/40%RDX	6,176,766	12,859,588	19,036,354
Composition C, 12%TNT/88%RDX	571,069	4,678,031	5,249,100
H-6	449,835	585,756	1,035,591
HBX	5,553,120	2,950,125	8,503,245
PBX	63,767	17,670	81,437
RDX	56,927	404,440	461,367
TNT	7,530,996	12,912,769	20,443,765
Tritonal	57,351,405	16,874,385	74,225,790

Table 2. Estimation of Current and Forecasted Tactical Missile Resource Recovery and Disposition Account Inventories (31 March 1999)

Type of Explosive	Current (lbs)	Forecasted (lbs)	Total (lbs)
COMP A-5, 99% TNT	0	1,148,960	1,148,960
COMP B	200,860	1,718,238	1,919,098
COMP B-4,	0	325,593	325,593
CYCLOTOL	24,850	160,448	185,298
DESTEX	131,795	1,014,800	1,146,595
H-6	225,200	706,230	931,430
HTA-3	16,487	106,646	123,133
OCTOL	285,365	3,238,926	3,524,291
PBX	3,750	22,500	26,250
PBXN-107	4,136	25,427	29,563
PBXN-109	142,416	870,228	1,012,644

In the current and forecasted munitions for demilitarization operations, there are 93 million and 40 million pounds of TNT and RDX, respectively, that are available for resource recovery, recycle, or disposition. This represents less than one percent of the total 538,436 tons of stockpile.

1.0 Laboratory-Scale Process

Preliminary work investigating the reactions between explosives and amines was done for Sandia National Laboratories by the IIT Research Institute, as reported in Appendix A. Several amines were reacted with the explosives TNT, RDX, and Comp B to find the optimum amine to decompose the explosives. Monoethanolamine, diethanolamine, diethylenetriamine (DETA), n-

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tributylamine, and ethylenediamine were all candidates. DETA is particularly interesting because it is the major constituent of DoD's decontamination solution for chemical agents, known as DS2. Thousands of tons of DS2 stockpile need destroying because it corrodes the containers in which it is stored. The potential application of DETA in DS2 for demilitarization of energetic materials, as well as chemical agents, is attractive and could substantially reduce the cost of the demilitarization. One requirement in selecting an amine was that the handling safety was well documented. The commercial product "Jeffamine" T-403 (polyoxypropylenetriamine, Huntsman Corp.), an amine curing agent used in 2-part epoxies, was chosen because it is commercial availability in large quantities, it has a low viscosity, and it has a well-documented safety record.

There are many considerations in choosing the optimum ratio of "Jeffamine" to be mixed with the explosive. One is a desire to consume as much explosive per unit of reacting agent as possible to destroy large quantities of surplus explosives. However, this produces a high-viscosity curing agent product, which is unworkable in the follow-on epoxy mixture. The ratio also affects the chemistry of the reaction and the production of N_2O (greenhouse) versus NO_2 (noxious) gases.

Several laboratory techniques were used to characterize the reaction between "Jeffamine" and the explosives. Laboratory-scale experiments were carried out on small quantities, 20 g or less of explosive. Running the reaction at temperatures lower than 120^oC resulted in very low reaction rates for TNT and Comp B, and no apparent reaction with RDX. Temperatures between 120^oC and 130^oC also resulted in long reaction times. It was found that reaction temperatures between 130^oC and 140^oC were ideal and resulted in manageable reaction rates without concerns of uncontrolled reactions taking place at higher temperatures due to explosive cook-off. Batch reactions were done in a 500 milliliter beaker on a stir/heat plate. "Jeffamine" was heated to $130°C$, then approximately 20 grams of explosive were added incrementally. After the chemical reaction, the modified "Jeffamine", crosslinks with an epoxy resin, such as Epon 828, and forms a mechanically useful epoxy.

1.1 Liquid By-Products

Epoxies produced by this method were found to be non-energetic as evident by thermal analysis, liquid chromatography, and burn tests. Mechanical properties of these epoxies were measured and found to be comparable to control samples of epoxy formed from conventional resins and curing agents.

Thermogravimetry (TGA) was used to determine the optimum temperature at which these reactions should take place. A typical TGA curve is shown in Figure 1. In this example, TGA was used to measure the weight loss of RDX, "Jeffamine", and a mixture of the two as they were dynamically heated at $10°C$/minute. A TA Instruments Simultaneous DTA/TGA was used for all runs. The sample size of the mixture was a nominal 12 milligrams (e.g., 2 milligrams RDX +10 milligrams "Jeffamine").

Figure 1 shows that the weight loss of RDX alone due to decomposition begins at approximately $210°C$. "Jeffamine" shows a gradual weight loss starting at $160°C$. When RDX is mixed with "Jeffamine," the decomposition reaction begins at a much lower temperature, 120 - $130°C$.

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Therefore, it was determined that 130°C was the optimum temperature to be used for all laboratory and scale-up reactions. A 1:4 ratio of RDX:"Jeffamine" was chosen for future experiments. The resulting modified amine curing agent has sufficiently low viscosity to allow processing an epoxy with good mechanical properties. The density of the virgin "Jeffamine" is 0.98 gram/cm^3, and the density of the liquid "Jeffamine" after reaction with the explosive is 1.03. With this ratio, there is approximately a 13% weight loss due to the gaseous decomposition of RDX.
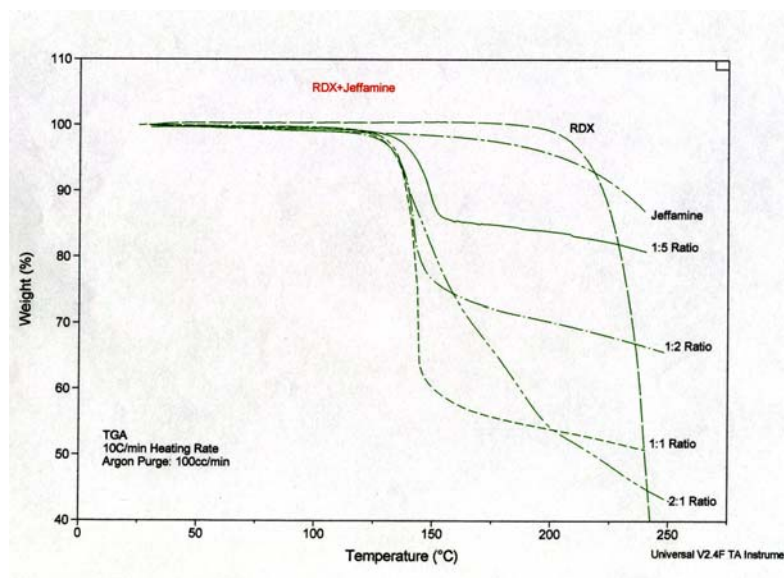
Figure 1. Weight Loss of RDX Added to "Jeffamine"

Using similar TGA experiments, the approximate ratios chosen for mixing "Jeffamine" with TNT and Comp B (60% RDX, 39% TNT, 1% wax) are 9:1 and 4:1, respectively.

As explosive is added to the hot "Jeffamine," it begins to foam due to the formation of decomposition gases in the viscous liquid. Surfactants were examined to determine their effectiveness in controlling this foaming. A few drops of surfactants, such as "X-Air", "Super Air-Out", or "Air Out" were added to the reaction vessel, to evaluate their ability to minimize this excessive foaming. "Air Out" worked the best and could be used to minimize foaming in future operations.

Figure 2 shows a typical differential scanning calorimetry trace with any exotherm, such as the RDX in Comp B decomposing at approximately 230°C, as a positive peak. Endothermic transitions, such as the TNT in the Comp B melting at 80°, are negative peaks. When Comp B is added to the hot amine, as in the second trace, there is a reaction exotherm of 468 calories per gram of explosive, peaking at approximately 145°C. This value of the heat evolved during this reaction was used to determine the cooling capacity necessary in the scaled-up reactor (section 2.1).

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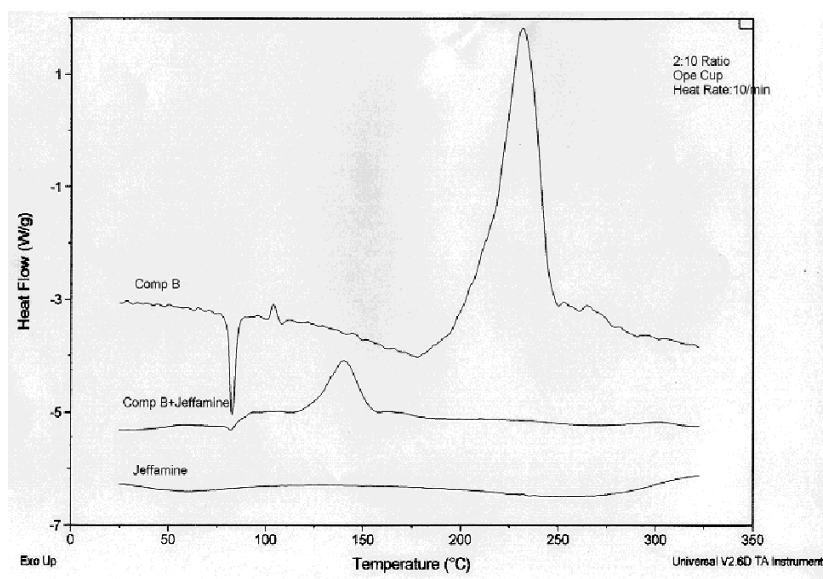
Figure 2. DSC Curve of Comp B and "Jeffamine"

Heat capacity measurements of the virgin "Jeffamine" were made using modulated differential scanning calorimetry. A 2910 model DSC made by TA instruments with a refrigerated cooling system was used. Argon was purged at 50 cc/min to displace the air in the DSC cell. The material was tested in a hermetically-sealed aluminum pan. Both the sample pan and the reference pan used in the DSC were within a weight variance of 0.5 mg. The unit was first calibrated for the heat capacity constant using a sapphire standard. The sample was heated from ambient to 200°C, ramping at 5°C/min, modulating +/- 1.00°C every 60 seconds. It was assumed that the heat capacity of the resulting reacted Comp B/Jeffamine solutions were similar to the heat capacity of virgin Jeffamine. These heat capacity values (Table 3) were used as input data to the computer modeling that was done on the scale-up calculations (section 2.2).

Progress was made towards the characterization of the colored reaction products of Jeffamine with TNT and RDX. Infrared analysis suggests that an amide is being formed as a result of the amine/RDX reaction. NMR analyses showed that in the case of RDX/amine interactions, the product contains amide groups formed as a result of charge transfer interactions between the amine and nitro group. In the case of the TNT/amine reactions, nucleophilic aromatic substitution takes place leading to the formation of Meisenheimer complexes and subsequent rearrangement to form C-N bonds[2].

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Table 3. Heat Capacity Values for Virgin "Jeffamine"

Temp (C)	Heat Capacity
	J/g/deg C
50	1.583
60	1.626
70	1.674
80	1.724
90	1.782
100	1.848
110	1.880
120	1.988
130	2.030
140	2.039
150	2.011
160	1.962
170	1.924
180	1.878
190	1.814

1.2 Gas Analyses

Gas chromatography was used to further define the optimum ratio of "Jeffamine" to be reacted with explosive. The goal was to determine a ratio of the two starting products, which would favor formation of N_2O (a greenhouse gas), rather than NO_2, which is a noxious gas regulated by the EPA.

Gaseous products formed during the reactions were analyzed by gas chromatography. A sealed stainless-steel chemical reaction tube (CRT) was used to react explosive with "Jeffamine". The reaction system was attached to a Hewlett-Packard gas chromatograph equipped with an internal gas-sampling valve and a combination thermal conductivity/flame ionization detector. Liquid nitrogen cooled the GC temperature to
-50^oC before the 20 C/minute heating ramp began. After reaction for the pre-determined time period, the CRT was opened, the pressure recorded, and the gas-sampling valve injected into the gas chromatograph for analysis of the evolved reaction product gases.
Figure 3 shows how varying the ratio of "Jeffamine"-to-explosive can vary the amount of N_2O formed. When this ratio is approximately 2 moles "Jeffamine":1 mole explosive, N_2O formation is enhanced (figure 2).

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Formation of N$_2$O upon mixing Jeffamine + Explosive

jeff + RDX
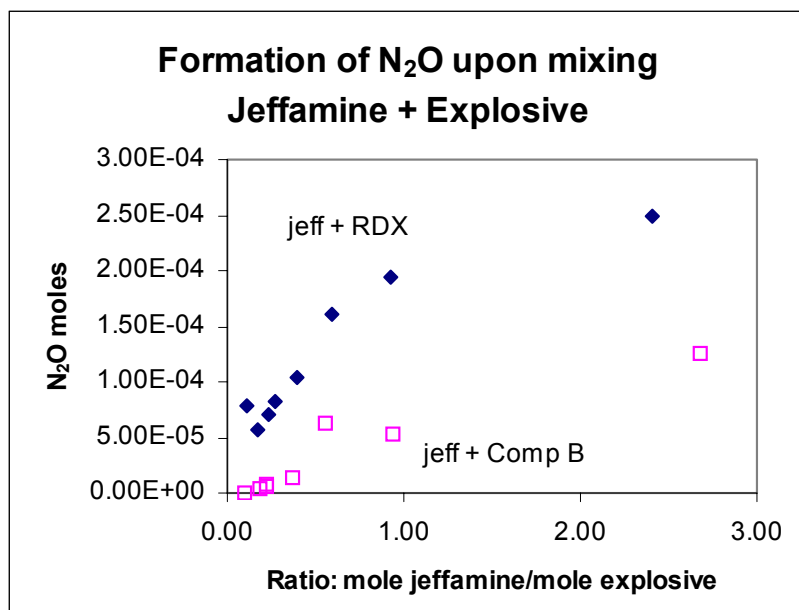
jeff + Comp B

Figure 3. Ratio of Jeffamine:Explosive to Achieve Maximum N$_2$O formation

To look at the contributions of the individual components of Comp B to the total gas evolved, RDX and TNT were reacted with "Jeffamine" separately. Figure 4 shows a typical gas chromatogram for the reaction between RDX and "Jeffamine." Notice the large nitrous oxide (N$_2$O) peak, which forms when RDX is the explosive.
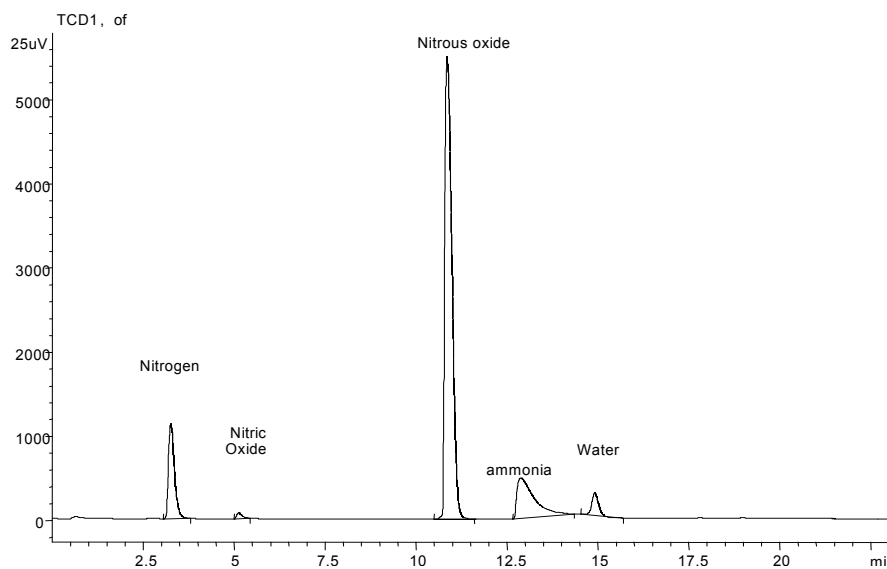
Figure 4. Gas chromatogram of RDX mixed with "Jeffamine" 130°C/1hr

Contrast this to the next figure to see the difference in the reaction stoichiometry when TNT is the explosive.

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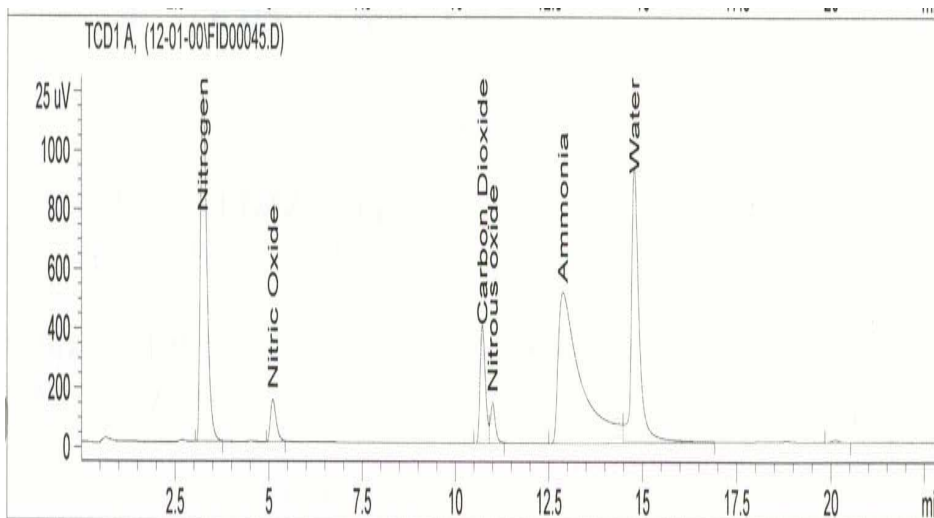
Figure 5. Gas chromatogram of TNT mixed with "Jeffamine" 130°C/1 hr

The fraction of N_2O (nitrous oxide) in the evolved gases is minimal when TNT is the explosive. Based on visual observations of tests mixing TNT and "Jeffamine", there is a considerable amount of brown gas formed, which would be NO_2. This gas is not detected by gas chromatography and, therefore, was not quantitated. Using "Jeffamine" to destroy TNT does not accomplish the goal of producing non-toxic gaseous by-products.

The amounts of six different gases formed during the reaction of "Jeffamine" with Comp B are plotted in Figure 6.
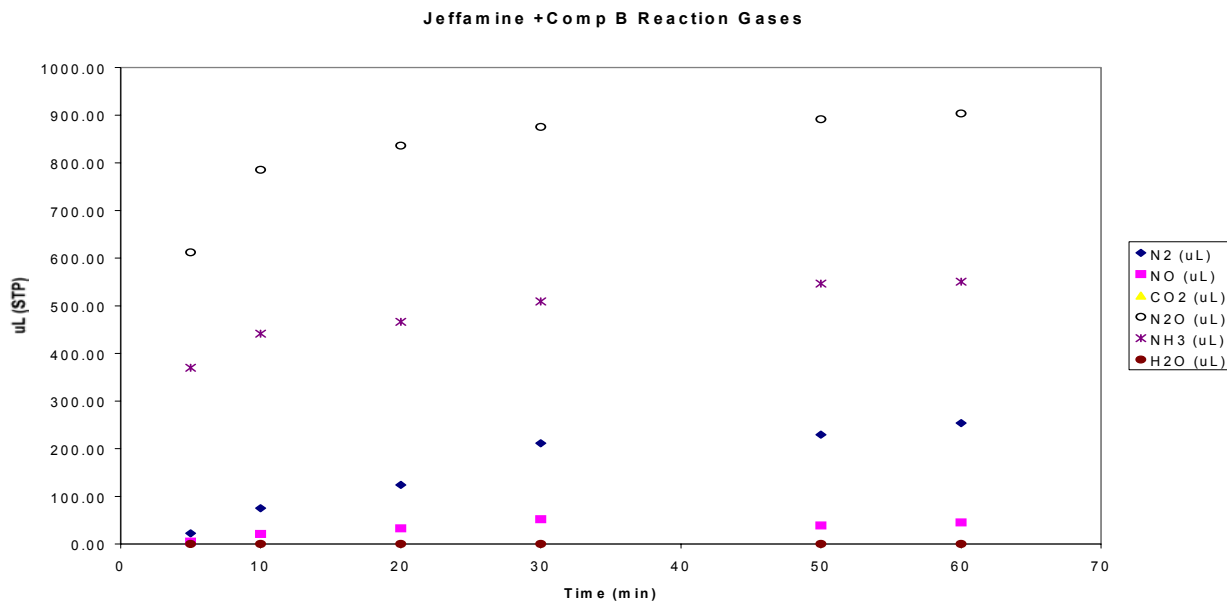
Figure 6. Gases formed during the Reaction of "Jeffamine" and Comp B at 130C.

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The amount of gas formed during the reaction of TNT with "Jeffamine" is shown in Figure 7. Notice the y-scale is different than that in Figure 6 and indicates that the amount of gas generated in this reaction is less than that in Figure 6. Although Comp B is 40% TNT, the majority of gases formed by the degradation is due to the RDX. Ammonia is a major component of the gases formed when TNT is the explosive, and it contributes 21% to the total ammonia formed when Comp B is reacted.
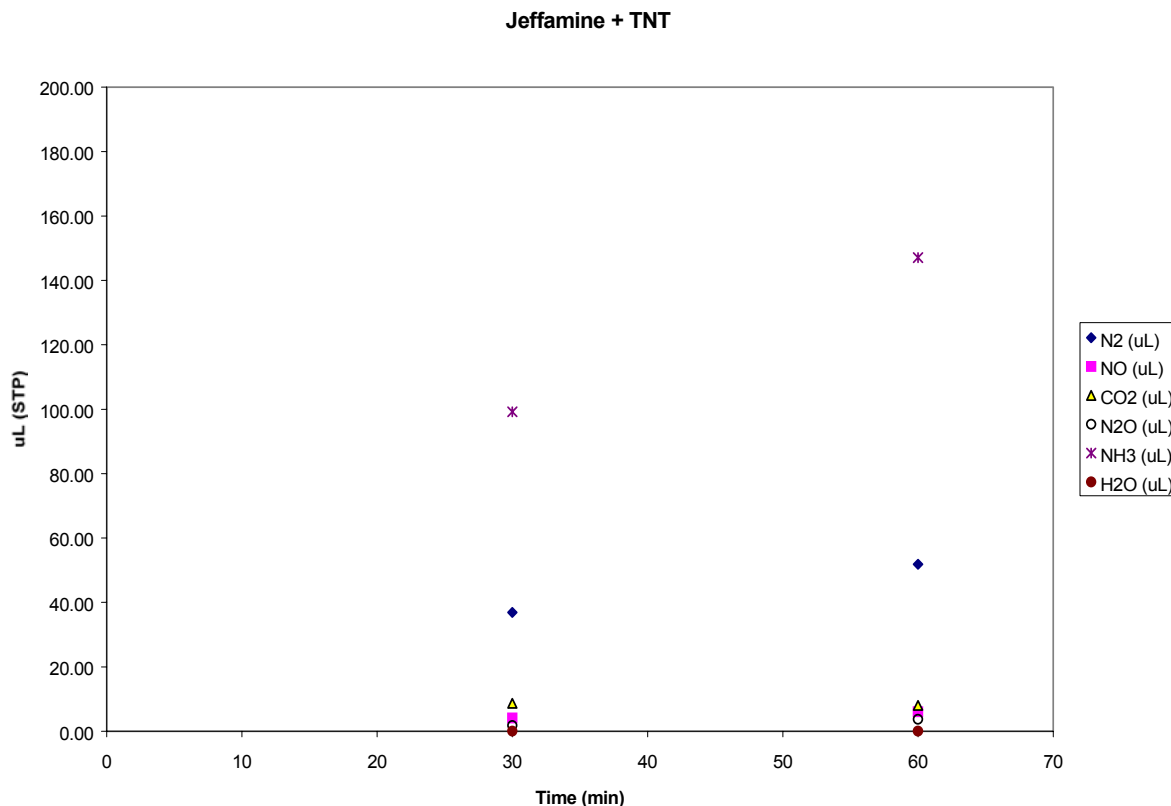
Jeffamine + TNT

Figure 7. Gases formed during the Reaction of TNT and "Jeffamine"

Based on gas quantities formed during the reactions, chemical reactions are presented which represent these degradation reactions:

- 1 mole Comp B $\rightarrow$ 0.5 N_2 + 0.09 NO + 1.8 N_2O + 1.1 NH_3 + .0001 H_2O + x_1NO_2

- 1 mole TNT $\rightarrow$
  0.26 N_2 + 0.03 NO + 0.02 N_2O + 0.73 NH_3 + .0002 H_2O + 0.04 CO_2 + x_2 NO_2

The values of x_1 and x_2 are unknown as the GC analyses could neither detect nor quantitate NO_2.

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Gases evolved during the reaction of RDX with the amine in an open beaker were carefully analyzed for escaping RDX vapor. A solid phase microextraction (SPME) fiber (polydimethylsiloxane/divinylbenzene, PDMS/DVB, Supelco, Inc. part no. 5710-U) designed to collect traces of explosives from air, was used. The fiber was held at various distances above the solution for a period of 10 seconds. After the collection period, the fiber was introduced into a PCP model 111 Ion Mobility Spectrometer and quickly heated to 165°C. The intensity of any resulting signal would be proportional to the concentration of RDX being released from the solution. A sample of "Jeffamine" alone did not produce a signal in the IMS. The concentration of RDX in the gases above the reaction mixture was measured at various positions. The concentration in all cases was less than that obtained from a sample of RDX when heated to that temperature.

1.3 Epoxy

Epoxies were made from the by-products of mixing "Jeffamine" T-403 and the three explosives, TNT, RDX, and Comp B (Figure 8). Epon 828 resin was heated at 71°C for 30 minutes. Silicone molds were coated with MS122 dry release agent and also heated at 71°C. The ratio of resin to modified-Jeffamine was varied, resulting in varied mechanical properties. The mixture was cured overnight at room temperature, followed by four hours at 71°C.

Epoxy
RDX/Amine
by-product

Epoxy
TNT/Amine
by-product

Figure 8. Epoxies made from Modified Amine Curing Agents

These modified epoxies were compared to standard batches of baseline epoxy which require 100 grams of preheated Epon 828 added to 41 grams of preheated curing agent. Testing was done to characterize both the baseline and modified epoxies.

Mechanical properties (shear modulus) and glass transition temperatures (T_g, when epoxies soften) for epoxy produced using the by-products were compared to those of epoxy produced with virgin "Jeffamine" curing agent. These tests were performed with a Rheometrics ARES Dynamic Mechanical analyzer using a torsion rectangular fixture at a frequency of 1 Hz and a temperature ramp rate of 3°C/min. The samples had nominal dimensions of length = 45 mm,

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width = 12.5mm and thickness = 1.3mm. A typical curve and scheme for selecting T_g of these samples is shown in Figure 9.

Scheme for Selecting Tg
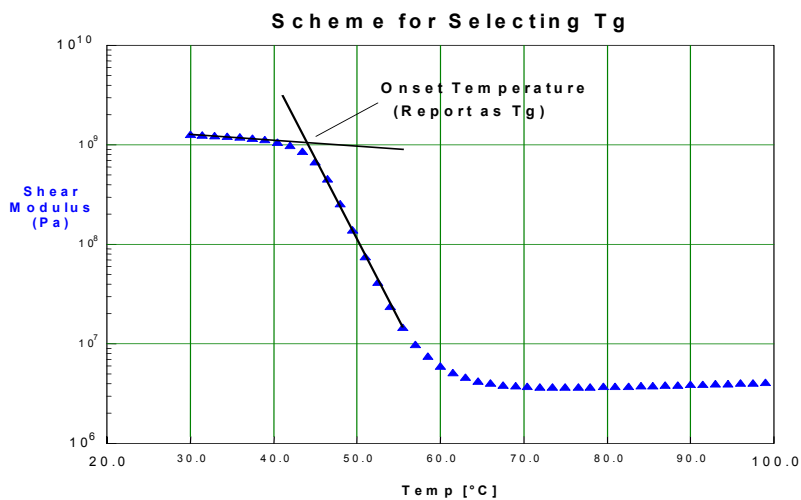
Figure 9. Typical curve for determining Glass Transition Temperature

Figure 10 shows the T_g's of epoxies made with varying concentrations of Epon 828 epoxy resin and "Jeffamine" T-403/RDX by-product. The right-most curve gives the T_g of baseline Epon 828 virgin/"Jeffamine" T-403 epoxy. This epoxy, made with 100g Epon resin and 41g "Jeffamine" T-403, softens at 71.4°C. When RDX is reacted with the curing agent, the T_g decreases. The left-most curve shows epoxy made with 100g 828 and 80g T403+RDX has a T_g at 27°C and is flexible at temperatures slightly above room temperature. Varying the concentration of the 2-parts of the epoxy can tailor the T_g for future epoxy applications.

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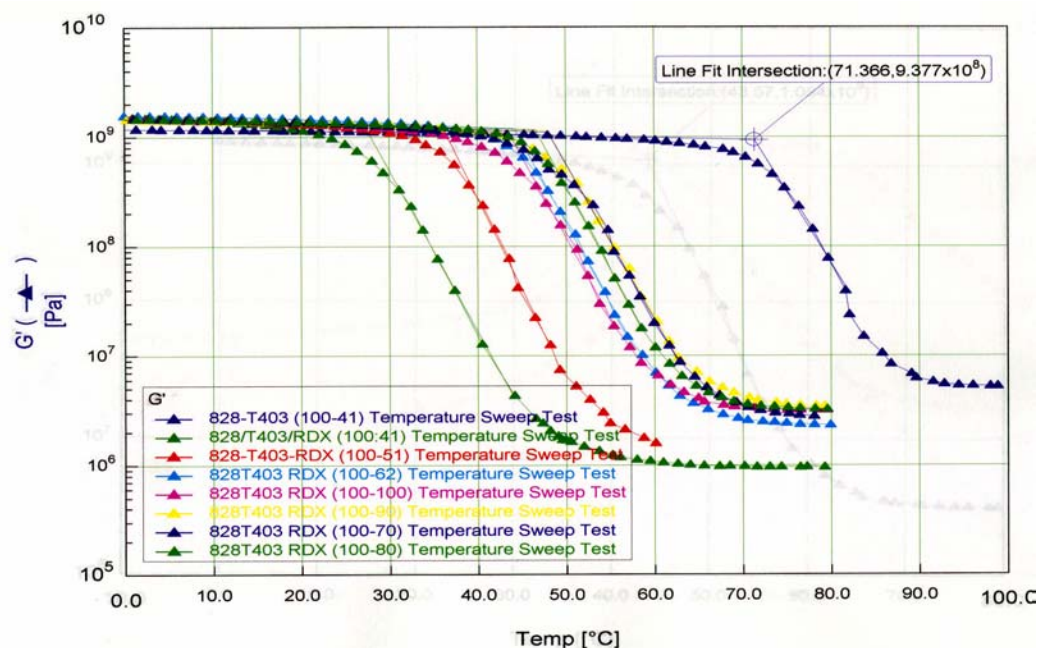
Figure 10. T_g of Epon 828 epoxies made with "Jeffamine"/RDX by-product

Figure 11 shows the T_g of Epon 828 epoxies made with "Jeffamine" curing agent modified with Comp B added at 15, 20, or 25%. The best ratio to mix Epon 828 and modified "Jeffamine" must be determined by the mechanical properties required for the final use of the epoxy.

Sample ID	Tg (C)
828/15% Comp B (25/25)	51
828/20% Comp B (25/25)	49
828/25% Comp B (25/25)	55
828/20% RDX (50/50)	44
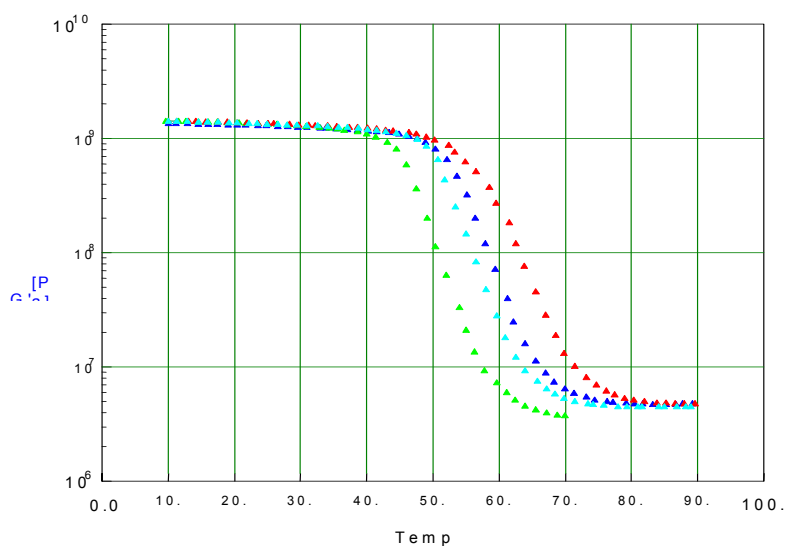
Figure 11. T_g of Epon 828 epoxy made with "Jeffamine"/Comp B by-product

These modified epoxies are intended for future commercial products and must be safe for persons handling the material. Therefore, the toxicity of these modified epoxies was investigated. The commercial, biosensor-based Microtox Toxicity system was used to test powders of epoxy samples prepared from a curing agent ("Jeffamine"), which was first reacted with RDX and with TNT. The Microtox test is based upon the use of luminescent bacteria, which produce light as a by-product of their cellular respiration[3]. Any inhibition of cellular activity due to toxicity results in a decreased rate of respiration and a corresponding decrease in the rate of luminescence. The more toxic the sample, the greater the percent light loss from the test suspension of luminescent bacteria. Bacterial bioluminescence has proved to be a convenient measure of cellular metabolism and consequently, a reliable sensor for measuring the presence of toxic chemicals in aquatic samples.

The baseline and modified epoxy powders were each mixed with water (2% NaCl) in glass centrifuge tubes to make 50% solutions. The mixture was shaken for 24 hours on a wrist-action shaker, then centrifuged for 15 minutes to extract water-soluble toxins. These solutions were then diluted down several times to a final concentration of 3% epoxy in water. The bioluminescence was measured at 5, 15, and 30 minutes after the bacteria were introduced.

The baseline epoxy powder solution was colorless, slightly cloudy, with a visible powdery gray film on the surface. The RDX/"Jeffamine" epoxy solution was colorless with a few very small orange crystals in the surface film. The TNT/"Jeffamine" epoxy solution was colorless without surface film. The concentration (in percent) of the epoxy solutions at which 50 percent of the illumination was quenched (EC_{50}) was determined to be as follows:

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Table 4. Toxicity of Epoxies in Water

Sample	5 minute EC_{50}	15 min EC_{50}	30 minute EC_{50}
baseline epoxy	13.5%	7.5%	4.9%
RDX epoxy	34.9%	16.4%	16.2%
TNT epoxy	35.3%	29.4%	23.7%

Baseline epoxy is toxic at a concentration of 13.5%. As the water extracts more chemicals from the epoxy over time, the solution is more toxic at 30 minutes, with a concentration of just 4.9% causing 50% of the bacteria to die. The RDX and TNT epoxies are actually less toxic than the baseline epoxy. Environmental criteria were established for TNT and RDX effluents with the allowable limits in aqueous discharge of 60 ppb and 200 ppb for TNT and RDX, respectively[4]. The "Jeffamine" epoxy toxicity results in Table II indicate that they less toxic by orders of magnitude, because these solutions do not become toxic until they are at the percent (%) level, rather than at the ppb level.

Flammability and shock testing of epoxy produced using the by-products indicated no explosive or flammability hazards. Velocity Interferometer System for Any Reflector (VISAR) tests were done to determine if the epoxies could be detonated. The VISAR has become the accepted standard for measuring particle velocities of shock loaded materials. Diffused light from the target containing Doppler-shift information is collected by a lens, split in half, with half of the signal being sent through a reference leg and half sent through a delay leg. A delay is caused between the two legs, and the beams are then recombined at the main beam-splitter where interference is developed. The target velocity information is contained in the motion of the interference fringes in each of the beams.

Epoxies made from modified "Jeffamine" were tested by shocking them with a PETN-boosted detonator to provide sufficient power to achieve a detonation in the epoxy, should sufficient explosive material still exist.

Three epoxies were tested:
> Virgin "Jeffamine" T403 only and 838 epoxy (control)
> 20% by weight TNT in the "Jeffamine" T403 and 828 epoxy mix
> 20% by weight RDX in the "Jeffamine" T403 and 828 epoxy mix.

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Table 5. VISAR Data for Cured Epoxies

Test Type	Unit Length (cm)	Function time (microsec)	Initial peak velocity (m/sec)
Baseline epoxy	70	32	22
Baseline epoxy	70	28	35
Baseline epoxy	70	30	30
20% by wt TNT	80	47	<10
20% by wt TNT	83	38	<10
20% by wt TNT	88	40	<20
20% by wt RDX	74	35	10
20% by wt RDX	80	40	15
20% by wt RDX	72	33	10

A detonation is determined by an initial peak velocity of 1000 m/sec or greater. The peak velocity and signature of the velocity data conclusively prove that none of the epoxy/explosive material detonated.

2.0 Process Scale-Up

A small scale-up operation was completed at Sandia National Laboratories to consume one kilogram of explosive. The waste explosive chosen for the scale-up operation was from the McAlester Army Ammunition Plant meltdown facility. The Comp B explosive is from shells such as 8-inch World War II battleship rounds and 105mm artillery projectiles. The shells are inverted and placed in heated and pressurized vats that melt the explosive[5]. The beige-colored liquid flows onto a chilled conveyor belt where it cools, hardens, then drops into cardboard boxes placed at the end of the belt. The explosive is now ready for reuse, recycle, or disposal. Fifty pounds each of melt-out TNT and Comp B were received from McAlester AAP for use in this study. These chunks are an appropriate size for a direct feedstock into the scale-up reactor.

The engineering parameters critical for scale up were evaluated. The gases evolved when the "Jeffamine" reacts with the explosive were characterized (section 1.2) to consider scrubbing these emissions in the final design. Gas chromatography analyses done on these gases show ammonia to be a relatively large component (10 – 20%), as is NO_2 when TNT is reacted, and both would be an air emissions concern in a large operation. Due to the small quantities involved in our studies, local Environmental Protection Agency requirements waived any scrubbing. However, upon future scale-up processes, the local requirements in that area would have to be consulted to ensure compliance.

2.1 Hardware

The reaction rate kinetics were determined to size the reactor. Thermogravimetric analyses were used to determine the weight loss due to gas formation. Samples of "Jeffamine" mixed with Comp B were heated at four different heating ramps (2.5, 5, 10, and 20 ^{o}C/min). The kinetics software on the TA Instruments TGA determined the activation energy, and preexponential

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factor, and a reaction time of 5 minutes. As decomposing the explosive in hot "Jeffamine" is quite fast, a vessel to accomplish this can be small. A 13 gallon aluminum vessel was fabricated and delivered to contain the reacting solution and foaming.

The scale-up process is a continuous operation, rather than a batch process. A conveyor belt carries the dry, chunk Comp B explosive up to the reaction vessel. This conveyor belt was chosen so that it could be added to the final step of an existing demil operation, such as that at McAlester Army Ammunition Plant. The conveyor is 9 feet long and 18 inches wide and has an anti-static polymeric belt, variable-speed drive, explosion-proof motor, and height adjustments. The control unit was mounted for remote operation. The conveyor belt delivered 1000g of Comp B explosive in 5 minutes (Table 6).

The ambient-pressure reaction vessel was designed and sized to meet two constraints. One is the net explosive weight limit of the building, 1000 grams in the test chamber. The reaction must proceed at a rate, which allows slow introduction of the explosive to ensure complete reaction. This influences the second constraint, which is the rapid removal of the heat generated by the reaction. A worst case was assumed to determine the temperature increase during a typical run, assuming 468 calories/gram of explosive. As our scaled-up reactions were limited due to building capacity, a 4 kW water chiller amply maintained constant temperature in the baffled water jacket surrounding the reactor during reaction.

Examples of processing times and feedstock rates to consume 1000 grams of explosive are shown in Table 6.

Table 6. Examples of Scale-Up Processing Parameters

Processing Time:	10 min	5 min	3 min
Comp B (g/min)	98	200	334
"Jeffamine" (g/min)	490	1,000	1,668
total volume (liters)	17.1	35.0	58.3
calculated heat generated (cal/hr) @ 468 cal/g explosive	2,752,941	5,616,000	9,360,000
kilowatts generated	3.20	6.53	10.88

The reactor was fabricated from aluminum because the thermal conductivity is higher than that of stainless steel, and allows better temperature control during the reaction. Calculations were done to design the side-wall baffles, impeller size, shape, and position. An air-driven motor stirs the vessel. The specifications for the custom reaction vessel (figure 12) were:

    Tank height: 27 inches
    stirrer: 3-bladed mixing propeller
    stirrer diameter: 5.5 inches
    stirrer offset from bottom: 2.75 inches (allowing for variable placement later)
    side baffles: 1 inch wide
    side baffles offset from bottom: 2.7 inches

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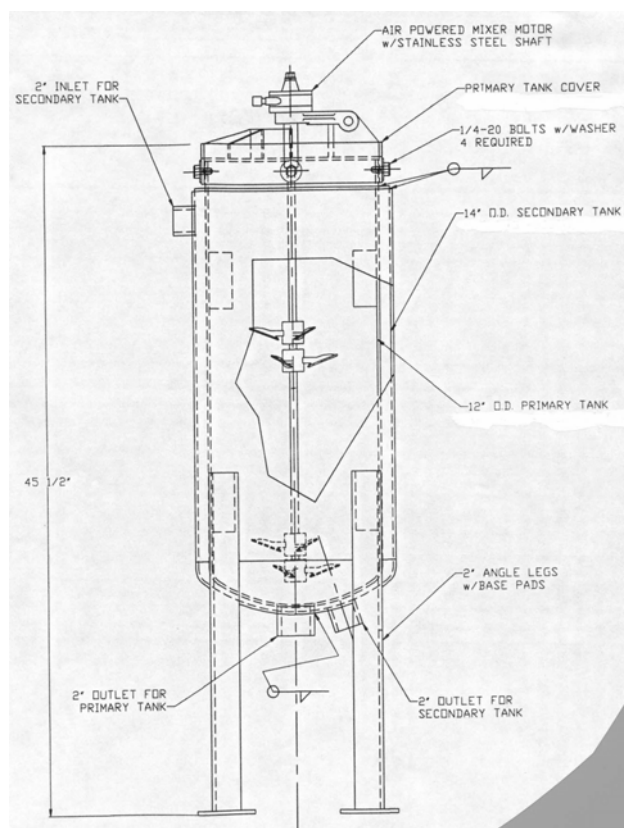
Figure 12. Drawing of Scale-up Reaction Vessel

Three small-scale safety tests were run to assure that during development of the scale-up process, a detonation would not occur during the addition of explosive to "Jeffamine." Assuming a worst-case scenario, each safety test had 100 grams of "Jeffamine" heated in a one-liter pyrex beaker at the operation temperature of 130°C in a chamber room rated to contain a 1 Kg explosion. Then, one 20 gram chunk of Comp B from the munitions melt-out facility at McAlester Army Ammunition Plant was added all at once using remote control.

The exotherm of the reaction ramped the temperature of the solution up to approximately 170°C, the solution foamed violently, but there was no detonation or fire. The temperature trace was tracked with an Omega Super MCJ Thermocouple-to-analog connector. This output was routed to a Tektronix TDS 784A Digitizing Oscilloscope where it was recorded. The experiment was also videotaped. Figure 13 shows the experimental set up, which was done using an empty steel tank as secondary containment.

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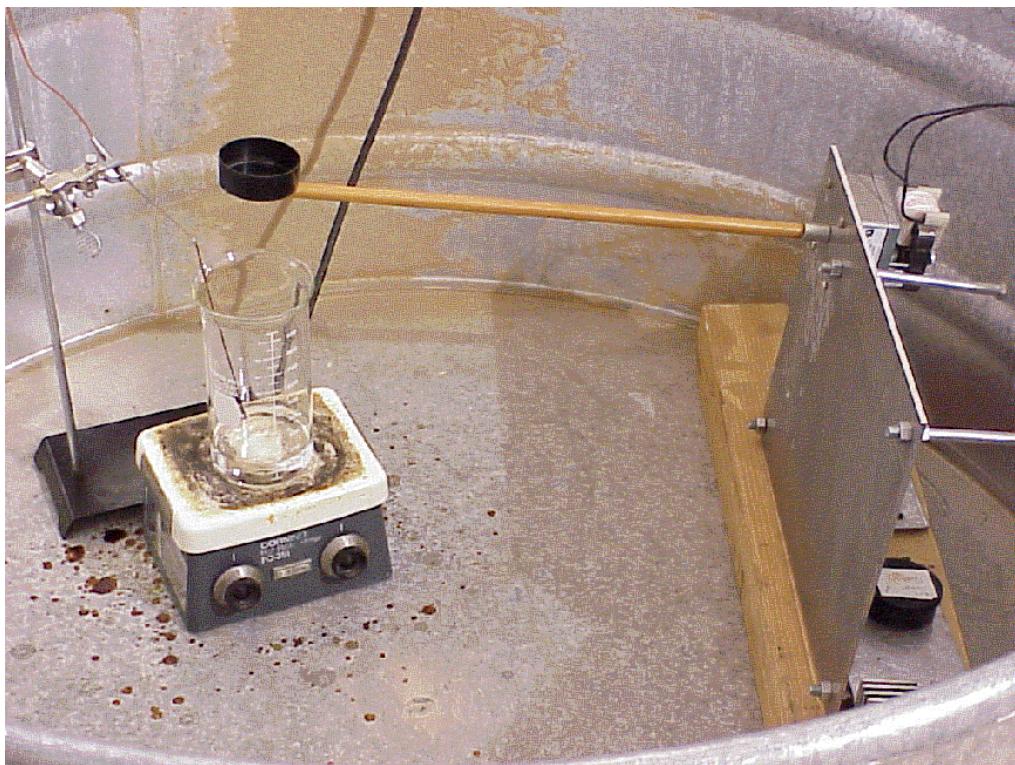
Figure 13. Equipment set-up for run-away reaction

In another experiment, a thermocouple was placed in the middle of a cylindrical cup and molten Comp B was added. Once cooled, this rod was removed from the mold, placed in another beaker of 130° C "Jeffamine", and the temperature was monitored during the reaction. Figure 14 shows the temperature traces of both the thermocouple embedded inside the Comp B rod and the thermocouple in the hot jeffamine solution when the chunk was added at 8.9 minutes.

(The anomaly in this experiment (lower line of plot) occurred because once the Comp B rod melted, the thermocouple fell out of the beaker at 11.5 minutes and began to cool, as seen at approximately 12.5 minutes.)

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Comp B + Jeffamine

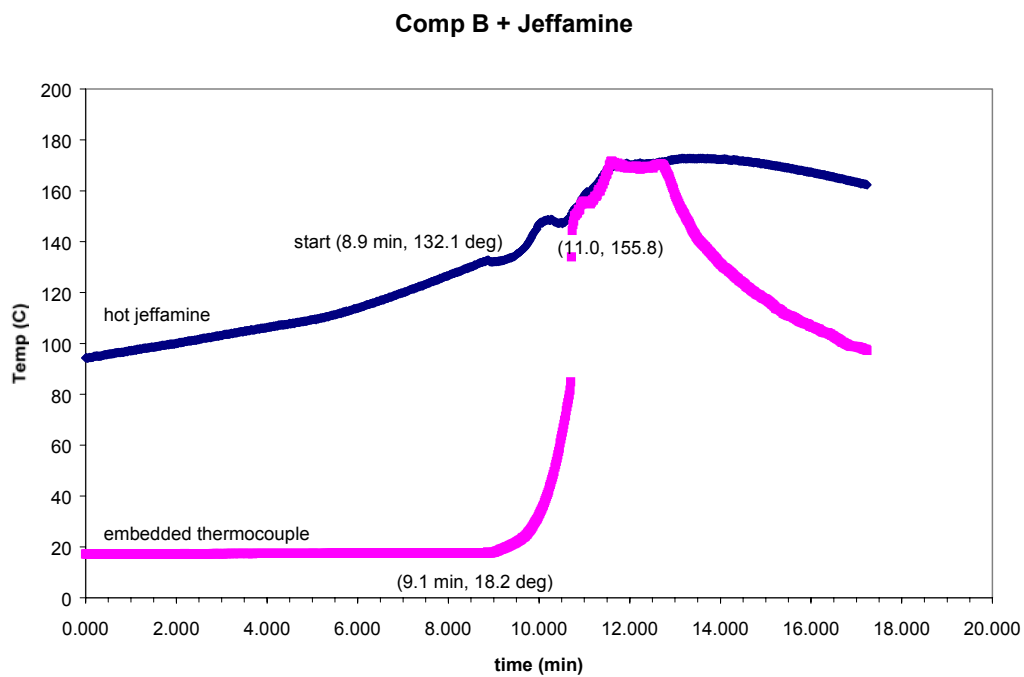*Figure 14. Typical Temperature profile of Safety test.*

The viscosity of the liquid by-product was determined to provide measurements for the pumping requirements for scale-up. The viscosity measurements were made from ambient temperature up to 150°C. Typical data are shown in Figure 15.
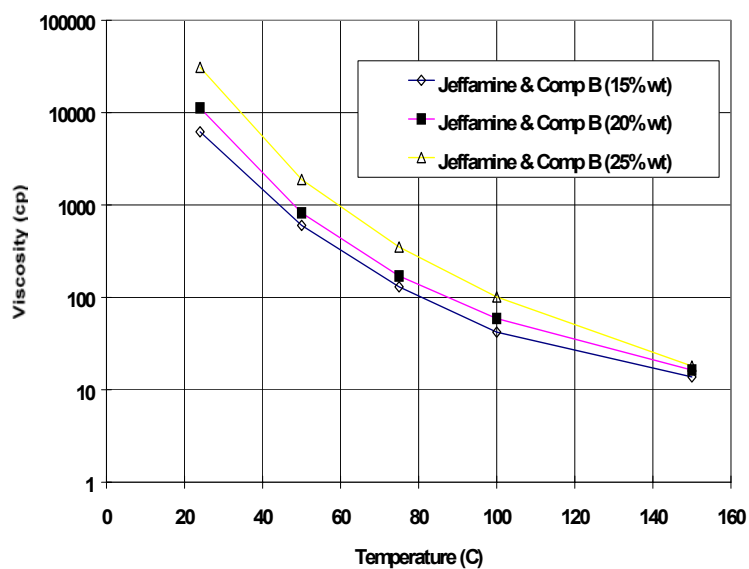
Viscosity Tests of Liquid By-Products

Figure 15. Typical Viscosity Data for By-Products

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The sequence of the scale-up operation starts with heating of the "Jeffamine" in its supply drum. An "Electro-Flex" band heater is wrapped around the metal drum and heated to 130° C. During that time, the explosive is measured onto the conveyor belt. Because the chamber limit at Sandia National Laboratories is 1000 grams of explosive, approximately 59 grams of explosive were weighed out and put in each of 17 pockets on the conveyor belt. The pumping rate of the "Jeffamine" supply drum pump (Teel Air-Driven, ½ HP) is 1 liter/minute. The reaction vessel exit pump (Teel Centrifugal, ¼ HP) was previously set to a flow rate that prevents accumulation of liquid reaction products during the continuous operation. The data logger is started, with four channels monitoring the temperatures of the cooling jacket inlet and outlet, "Jeffamine" supply drum, and reaction temperature. The blast door to the chamber is closed and the stirrer started at 300 rpm. At time zero, the "Jeffamine" pump is started, then the conveyor belt; both run for five minutes. The reaction vessel exit pump is started to pump out the reacted liquid. The gases evolved are drawn out of the room with an exhaust fan. Samples were taken from the reaction vessel and analyzed for residual explosives by high performance liquid chromatography. None was found, indicating that the scale-up process can be done satisfactorily.

2.2 Computer Modeling of Process

The chemistry and heat production within the scale-up vessel was computer modeled to ensure complete reaction and safety during processing. A consulting contract with CFD Research Corp., Huntsville, Alabama provided computation of the flow, heat generation, heat transfer, and mass transport in the system. This model may be easily adapted for other complex geometries and process parameters. The final report from CFDRC is found in Appendix C.

The approach to modeling the Sandia reactor will be to couple the one-phase and chemistry modules in the multi-physics code, "CFD-ACE". The code computes the flow, heat generation, heat transfer and mass transport in the system as part of the solution. The reaction mechanisms were supplied by Sandia. The developed model may be easily adapted for complex geometries and process parameters. It will allow the process engineer to evaluate the potential of over heating and reaction efficiency for a given reactor design and set of operating conditions.

The foundation for the model is the general purpose, commercial computational fluid dynamics code, CFD-ACE, which is a transient, three-dimensional, Navier-Stokes code capable of simulating multi-species transport, heat transfer (including thermal radiation, fully coupled gas-phase and surface chemistry for conventional chemical vapor deposition (CVD) reactors. The CFD-ACE package is a very flexible code, that is coupled with preprocessing and post processing software (CFD-GEOM and CFD-VIEW) that make it relatively straight-forward to set up models for complex geometries and analyze the results. The complete report can be found in Appendix C.

3.0 Technology Transfer

3.1 Economics of Degrading Bulk Explosives

Transferring this technology to another government or commercial organization was investigated. An advertisement seeking a partner to use the by-product-"Jeffamine" or to further develop the process was published in the Commerce Business Daily (see Appendix B). No responses were received.

The price of degrading explosives by this method is rather high, however, at a cost of $21,000 per ton of explosive. This is estimated based on buying "Jeffamine" at $2.19 per pound from the Huntsman Petrochemical Corporation, Houston, TX., USA., assuming no cost for the explosive, and loading it with 20 percent waste explosive. There would be some payback if commercial uses for the liquid or gaseous by-products could be found.

A minimal payback of this process could recover nitrous oxide for later sale. N_2O is a valuable chemical in some oxidation reactions of benzene and its derivatives to phenols, and it has use in the medical and dental fields[6]. There are zeolite molecular sieves which are available to adsorb N_2O, for later desorption. The water (steam) venting from the process would be passed through a γ-Al_2O_3 bed to be absorbed before traveling to the molecular sieves. Barium-exchanged ZSM-5 zeolites trap the nitrous oxide[7,8] from $25 - 80^oC$, then desorb the gas at $150 - 220^oC$. These zeolites could be reused after desorbing the N_2O. On a large scale of processing tons of explosives, the reusable N_2O-stripping bed would require 26,300 lbs of zeolites, a one-time cost at the current price of $55/lb. The economic payback of reclaiming the N_2O would only be approximately 2.4% of the cost of processing the explosives.

There are other resource recovery technologies[1] that can recover the TNT and RDX for resale. While private industry is paying $6 - $7/lb. for virgin RDX Class I, ANFO boosted with RDX sells for $1/lb[9,10]. TPL, Inc. has demonstrated 150lb/day plant at Ft. Wingate, N.M., for recovery of RDX from CompA-3. AMCOM proposed to qualify reclaimed RDX for reformulation and casting into recycled rocket motor hardware. Mechanical property, ballistic and static motor firings will be performed for the reference and reclaimed propellant formulations. Eglin AFB has developed a method for the recovery of TNT and RDX from melt/cast explosives such as Comp B and Octol. ARDEC is developing processes to rework downloaded explosives to meet specification requirements for military as well as reformulate into products for potential commercial market applications. Lawrence Livermore National Laboratory has developed a lab-scale synthesis to convert TNT to higher value products such as TATB.

3.2 Firing Range Clean-Up

Due to this high cost of processing bulk explosives, this technique was considered for environmental clean up for firing ranges and range sustainment. Low-order-detonation shrapnel from 105 mm shells fired on Sandia's remote range was picked up and placed in a beaker of hot "Jeffamine". A seven-minute soak cleaned sub-gram amounts of explosive from the metal parts (Figure 16), leaving just nanogram-level traces of explosive on the metal surface. Agitation of the solution or a high-pressure spray would shorten the cleaning time. Firing ranges could be

cleaned with a portable tank of hot "Jeffamine" mounted on a truck with shrapnel placed in a basket immersed in the liquid. An example of fragments to be cleaned can be found on Hawaii's Kaho'olawe Island, which was a firing range until 1995 (Figure 17).

Figure 16. 105 mm shrapnel before and after soaking in "Jeffamine". White material on the two left pieces is the explosive before cleaning; the right pictures are after cleaning.

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Figure 17. Kaho'olawe Island, Hawaii

4.0 Conclusions

This process completely degrades RDX, TNT, and Comp B by reacting them with an amine, "Jeffamine", a commercial product. The purity of the explosives required to accomplish this degradation was not established. However, melted-out explosive material from old munitions was used as-received from McAlester Army Ammunition Plant.   The goal was to determine the best stoichiometry and reaction conditions to accomplish degrading as much explosive as possible, using the least amount of "Jeffamine". The results show that "Jeffamine" can be loaded with approximately 25% explosive to accomplish the complete destruction of the explosive. The composition of the gaseous products can be varied by the stoichiometry to influence the amount of noxious gases. The chemistry of reacting "Jeffamine" with RDX produces more nitrous oxide (N_2O) than reacting it with TNT. Comp B (60% RDX, 40% TNT) is also consumed by this process, but the presence of TNT increases the amount of NO_2 formed during the chemical reaction.   Safety tests were performed to ensure that the reactions, which are very exothermic, were safe and that no detonations or run-away reactions took place. The liquid by-product of these reactions can be used as a curing agent with an epoxy, such as Epon 828. The mechanical properties of epoxies made from the liquid by-products can be tailored for future applications.

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The reaction was scaled up to process 1000 grams using Comp B and TNT from the McAlester Army Ammunition Plant meltout facility. Computer modeling computed heat flow, generation, and transfer, and mass transport to predict scale-up parameters for even larger scale-up operations.

The economics of this process indicate that the cost of degrading one ton of explosive is approximately $21,000. Minimal payback could be realized with the recovery of the nitrous oxide produced during the reaction, and any sale of the liquid by-product for use in epoxies, if a customer could be identified.

Due to this high cost of processing bulk explosives, the process could be used instead for firing range clean up and sustainment and processing of smaller quantities of explosive materials when other disposal means are not feasible or economical. A portable vat of hot "Jeffamine" could be transported around a contaminated field, with a basket of shrapnel immersed in it to clean off residual explosives.

Acknowledgments

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5.0 References

1) Wheeler, James Q., et. al., "Joint Demilitarization Study", Joint Ordnance Commanders Group Munitions Demil/Disposal Subgroup, July 1999,

2) personal correspondence from Darryl Sasaki, Sandia National Laboratories.

3) MicroTox Toxicity Testing Procedure, instrument manual, ToxScan, Inc., Watsonville, California.

4) Rodacy, P. J., et. al., "Destruction of Explosives in Groundwater and Process Water Using Photocatalytic and Biological Methods", Sandia National Laboratories, SAND96-0929.

5) Kennedy, Harold, "Demilitarization Work Takes its First Budget Hit in Years", National DEFENSE, July/August 1999, pp. 35-36.

6) Centi, G., Perathoner, S., and Vazzana, F., "Catalytic control of non-CO_2 greenhouse gases", *Chemtech*, December 1999, p 48.

7) Marcus, B., and Cormier, W., "Going Green with Zeolites", Zeolyst International publication.

8) Centi, G., Generali, P., dall'Olio, L., Perathoner, S., and Rak, Z., "Removal of N_2O from industrial gaseous streams by selective adsorption over metal-exchanged zeolites", *Industrial & Engineering Chemistry Research*, January 2000, v. 39, pg. 131.

9) communication with BAE Systems Ordnance Systems Inc., Holston Army Ammunition Plant.

10) communication with Ensign-Bickford Aerospace and Defense.

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6.0 Appendix A – IITRI Report

"Hypergolic Non-Detonative Neutralization of Energetics in Production and Demilitarization"

(The electronic version of this master document has a separate file attached that contains this IITRI Report. The hardcopy has the text included)

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7.0 Appendix B – Commerce Business Daily Ad

[Commerce Business Daily: Posted in CBDNet on June 8, 2000]
From the Commerce Business Daily Online via GPO Access
[cbdnet.access.gpo.gov]

PART: SPECIAL NOTICES
OFFADD: Sandia National Laboratories, Technology Partnerships
      Dept., PO Box 5800-MS1380, Albuquerque, NM 87185-1380
SUBJECT: MODIFIED "JEFFAMINE" T-403" AMINE CURING AGENT
      FOR EPOXY FORMULATIONS
DESC: Sandia National Laboratories has a laboratory-scale chemical process which produces a by-product of modified "Jeffamine" T-403" (commercial product of the Huntsman Corp.). "Jeffamine" T-403" is a trifunctional amine used as a curing agent for epoxies such as Epon 828. Sandia's patented process utilizes the virgin "Jeffamine" T-403" to degrade explosives such as TNT and Comp B into safe products. "Jeffamine" T-403" is used as a reactant in the chemical reaction, then, after reacting, the modified-"Jeffamine" becomes part of the waste stream. This non-explosive, off-color, viscous "Jeffamine" by-product can still be used to make epoxy for use in applications which do not require virgin "Jeffamine"." Epoxies made with this modified "Jeffamine" have altered mechanical properties, such as lower glass transition temperatures. However, the mechanical properties can be tailored for use in the final epoxy application.
  This chemical process is one of military interest. The Department of Defense and Department of Energy have funding to dispose of hundreds of thousands of tons of ammunition during the next decade. About 100,000 tons/year of new materials are added to this inventory. The huge inventory of obsolete military explosives are available for this process and will provide many tons of modified "Jeffamine" T-403" for commercial applications.
  Sandia is interested in identifying potential users of the modified "Jeffamine" T-403" amine curing agent and/or partnering with a commercial company to scale up the operation from laboratory scale to industrial proportions. Demilled explosives are available from Army Ammunition Plants to demonstrate the process and scale-up.
EMAILADD: slpound@sandia.gov
EMAILDESC: Sheila L. Pounds
CITE: (W-160 SN462822)

8.0 Appendix C – CFD Research Final Report

**DEVELOPMENT OF A NUMERICAL SIMULATION TOOL
FOR THE
SANDIA ENERGETIC MATERIAL NEUTRALIZATION PROCESS**

Final Report

**By
Debasis Sengupta, Maryam Shariati, and Sam Lowry
CFD Research Corporation
215 Wynn Drive
Huntsville, AL 35805**

April 2001   **CFDRC No.: 8313/2**

ACKNOWLEDGMENTS

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1.   BACKGROUND

Sandia National Labs is investigating an alternative environmental technology to replace open burn/open detonation (OB/OD) operations for the destruction and disposal of obsolete, excess, and off-spec energetic materials. Organic amines have been found to chemically react with explosives like TNT, RDX and Composition B (60%RDX, 40%TNT, wax), safely breaking them down without detonation. The reaction creates liquid products that are effective curing agents for conventional epoxy resins. These epoxies are safe and non-detonable and their commercial use will be explored to complete the recycle of the explosives.

In support of this project, CFD Research Corporation has developed a model of the above neutralization process. This model has been used to analyze the effects of scale-up and operating condition on the maximum temperature obtained during the reaction. The maximum temperature and time are two critical parameter since it indicates the potential for explosion. The model development and conclusions are presented in this report.

2.   TECHNICAL APPROACH

The modeling in this project was to adapt the multi-component chemistry option in the CFD-ACE to simulate the foaming reaction in the Sandia reactor. The code computes the flow, heat generation, heat transfer and mass transport in the system as part of the solution. The reaction mechanisms were developed and calibrated based on experimental data from Sandia. A series of simulations was subsequently performed to investigate the effects of geometry, initial conditions, and boundary conditions on the reaction process.

3.   EMPIRICAL DATA

Sandia National Laboratories have been experimentally investigating the neutralization of explosives using Jeffamine. A partial overview of these experiments, as they relate to the modeling effort, is provided in this report.

Sandia's initial work in FY99 was on a laboratory-scale. This work confirmed that the commercially available "Jeffamine T-403" (product of Huntsman Corp.), an amine curing agent used in 2-part epoxies, is effective in decomposing explosives such as RDX, TNT, and Comp B. The experimental investigation was performed in a 1000-milliliter tall pyrex beaker. After Jeffamine was heated to 130C and stirred with a magnetic stirrer, a small quantity of fine powdered explosive (up to 20g) was added either incrementally or "all-at-once". Different scenarios were tested to determine the possibility of a worst-case thermal run-away that leads to detonation of the mixture. Such scenarios (behavior of the exothermic reaction) are directly related to the safety of the scale-up process that is needed for the effective decomposition of the explosives. The laboratory-scale experiments revealed a complicated sequence of events that led to intense foaming, and the production of gaseous and liquid products. Differences in the final color of the liquid products seem to indicate that the chemical pathway and final products are affected by the type of explosive added to the Jeffamine. Gaseous products have been collected and

analyzed using gas chromatography.   Typical results for the reaction of RDX and Jeffamine are presented in Fig. 1.
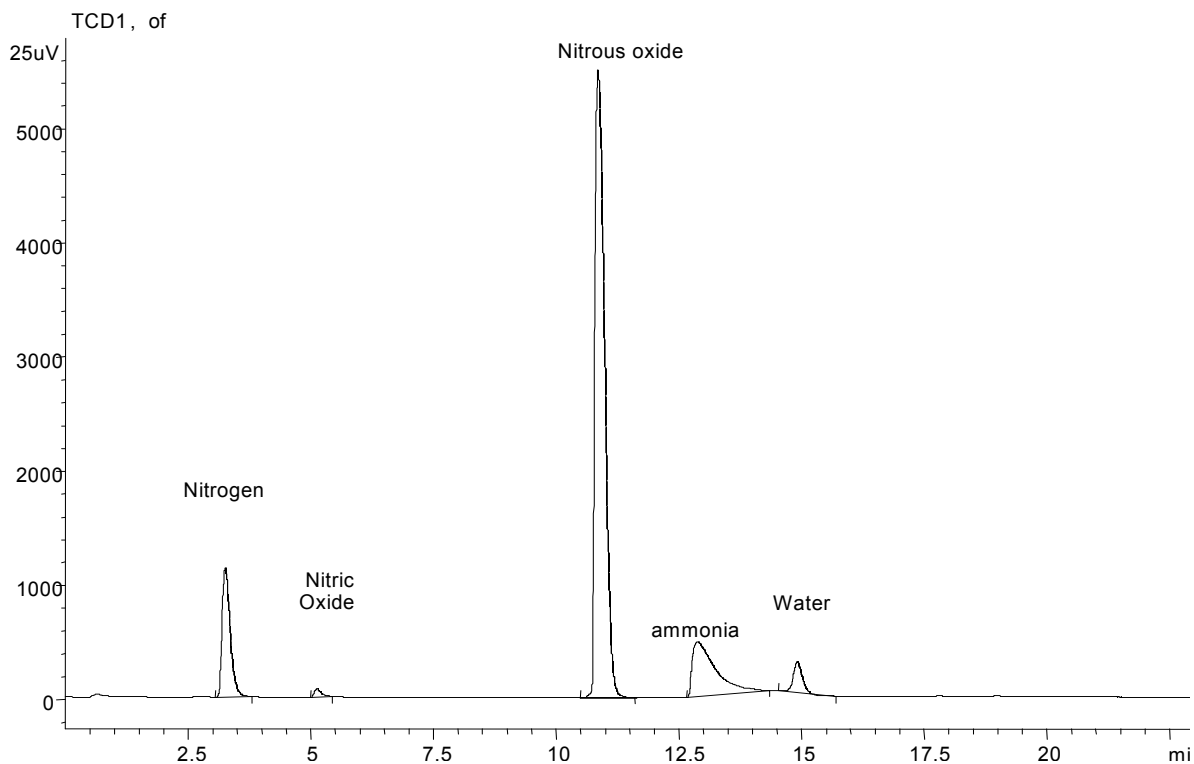
Figure 1. Reactant Products for the Reaction of RDX and Jeffamine

Following the FY99 experiments, additional experiments were conducted for "chunks" of Compostion B and TNT dropped into pre-heated Jeffamine. Table 1 provides the test matrix for one of these tests series. As before, the experimental investigation was performed in a 1000-milliliter tall pyrex beaker. After Jeffamine was heated to 130C using a hotplate, the chunks were dropped into the heated liquid. Throughout the process, the mixture is stirred with a magnetic stirrer. The addition of the room temperature chunks temporarily lowers the average temperature of the Jeffamine. As the chunks melt and the temperature of the liquid mixture re-establishes 130C, the hotplate is turned off. Figure 2 shows a schematic of this experiment. Figure 3 provides the temperature profiles for the four cases in Table 1 based on a thermocouple dipped into the liquid.

Table 1. Test Matrix for the Reduction of TNT and Compound B in Jeffamine

Curve	Explosive Material	Diameter of Chunk	Mass (in grams)
A	Comp B	1 inch rod	23.8
B	Comp B	1 inch rod	26.6
C	Comp B	Wafer like	23.8
D	Comp B	1 inch rod	29.9
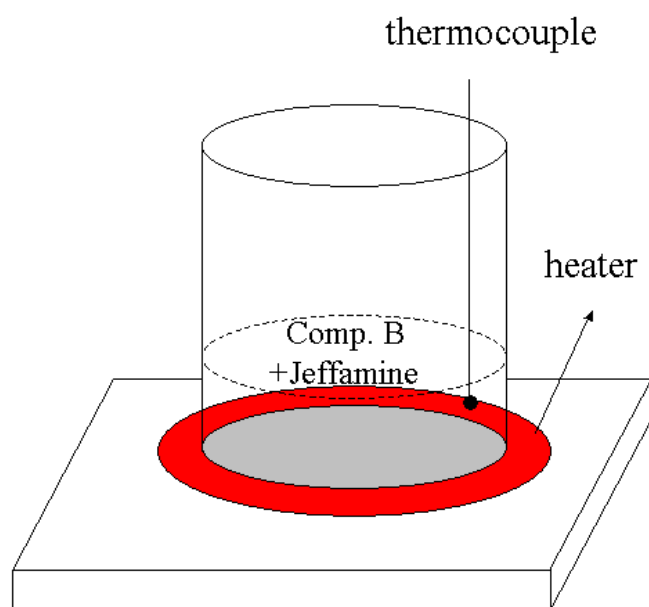
Figure 2. Schematic for the Reduction of TNT and Comp. B
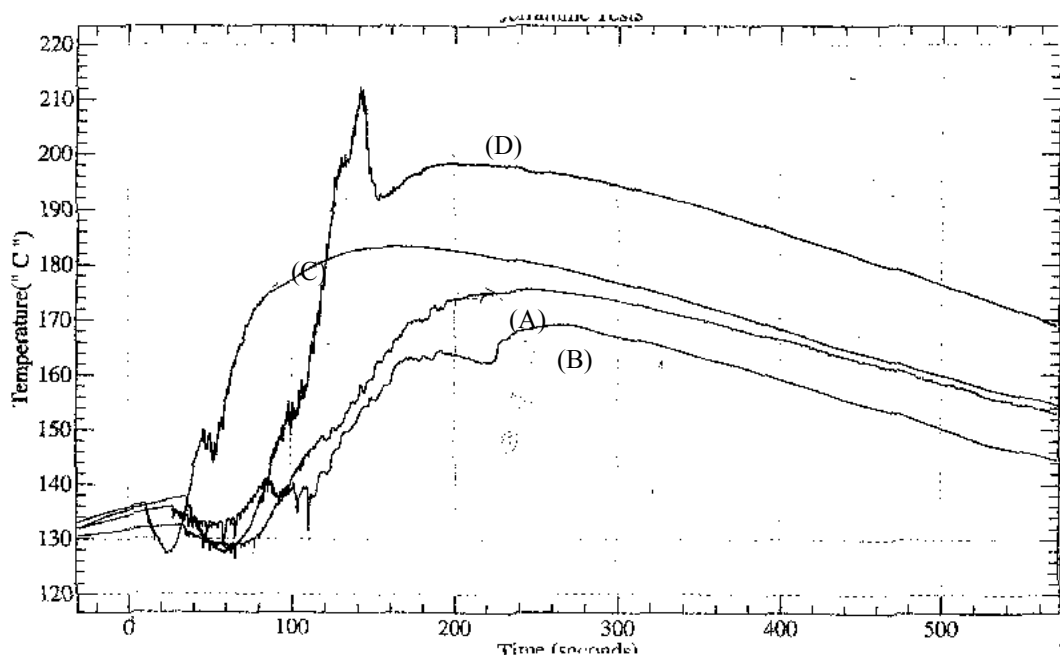
Figure 3. Thermal histories for reduction of Comp. B

The procedure used in the above experiments is similar to the proposed procedure for the full-scale process. However, it is too complex to facilitate model calibration in the sense that too many processes occur simultaneously. For example, the chunks are being stirred and melt as the reaction occurs. At the same time, the hot plate is providing heat to the beaker in an uncontrolled manner. This makes the problem a three-phase reaction with unknown boundary conditions. In order to simplify the modeling calibration, Sandia National Labs conducted a more controlled experiment. This experiment was described as follows:

"This was another glass beaker experiment, with 100 grams of Jeffamine heated to 77C. Then 20 grams of powdered Comp B were added while the hot plate was still on. Once the temperature of the reacting solution reached 130C, the heater/stirrer was turned off.

There were 4 thermocouples in place: one in the reacting solution, one at the 425 ml level (of the 1000 ml beaker), one at the 600 ml level, and one tucked under the edge of the beaker and taped to the hot plate. Some of the reaction took place between 77 and 130C, so the foaming was not as severe as in previous experiments."

The results of the experiment are provided in Figure 4.

5

Measurement of Foam and Hot Plate Temps
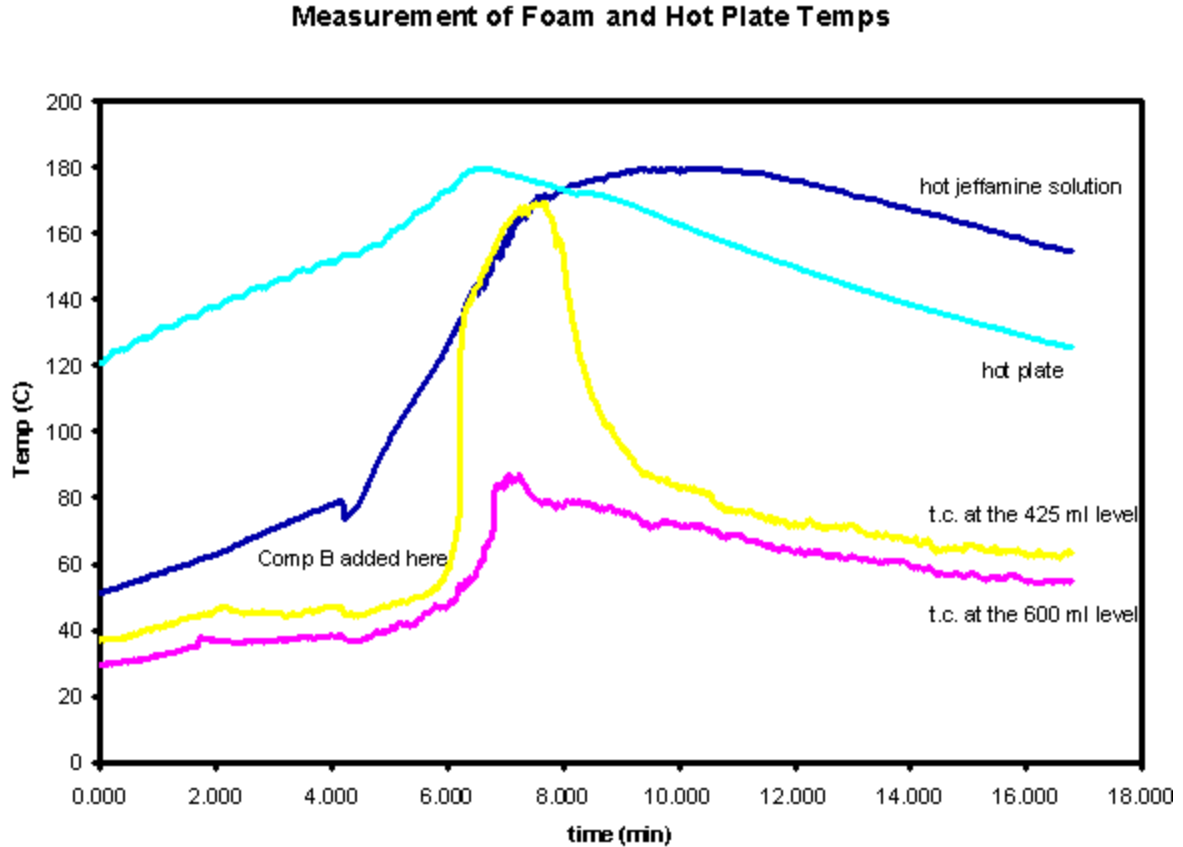
Figure 4. Thermal Histories for Reduction of Comp. B Using a Slow Heating Process

4.0   DESCRIPTION OF THE NUMERICAL CODE AND PHYSICAL MODELS

The foundation for the model is the general purpose, commercial computational fluid dynamics code, CFD-ACE, which is a transient, three-dimensional, Navier-Stokes code capable of simulating multi-species transport, heat transfer (including thermal radiation, fully coupled gas-phase and surface chemistry for conventional chemical vapor deposition (CVD) reactors. The CFD-ACE package is a very flexible code, that is coupled with preprocessing and post-processing software (CFD-GEOM and CFD-VIEW) that make it relatively straightforward to set up models for complex geometries and analyze the results.

4.1   Basic Features of CFD-ACE Code

The governing equations that are solved by CFD-ACE are:

Mass:
$$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{u} = 0 \tag{1}$$

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Momentum:
$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot \rho \mathbf{u}\mathbf{u} = -\nabla p + \nabla \cdot \boldsymbol{\tau} + \rho \mathbf{g}$$
(2)

Energy:
$$\frac{\partial \rho h}{\partial t} + \nabla \cdot \rho \mathbf{u}h = \nabla \cdot \mathbf{q} + \boldsymbol{\tau} : \nabla \mathbf{u} + \frac{dp}{dt}$$
(3)

Species:
$$\frac{\partial \rho Y_i}{\partial t} + \nabla \cdot \rho \mathbf{u}Y_i = \nabla \cdot \mathbf{j}_i + \dot{w}_i$$
(4)

where ρ, $\mathbf{u}$, p, h Y_i are density, velocity, pressure, enthalpy and species mass fraction, respectively. w_i is species production rate due to gas-phase reaction.

Shear Stress:
$$\boldsymbol{\tau} = \mu\left(\nabla \mathbf{u} + \nabla \mathbf{u}^T\right) - \frac{2}{3}\mu(\nabla \cdot \mathbf{u})\mathbf{I}$$
(5)

Diffusive Energy Flux:
$$\mathbf{q} = \lambda \nabla T + \sum_i h_i \mathbf{j}_i$$
(6)

Diffusive Species Flux:
$$\mathbf{j}_i = \mathbf{j}_i^c + \mathbf{j}_i^T$$
(7)

Stefan-Maxwell Diffusion:
$$\mathbf{j}_i^c = \rho D_i \nabla Y_i + \frac{\rho Y_i}{M} D_i \nabla M - M\sum_j D_j \nabla Y_j - \nabla M \sum_j D_j Y_j$$
(8)

(M is the mixture molecular weight)

Soret Diffusion:
$$\mathbf{j}_i^T = \frac{\rho D_i^T}{T}\nabla T - \rho Y_i \sum_j \frac{D_j^T}{T}\nabla T$$
(9)

4.2   Chemistry

Very complex chemistry is currently available in the single fluid module of the CFD-ACE code. This chemistry may be comprised of multi-step finite rate reactions of the form:

$$\frac{\partial}{\partial t}(\rho Y_i) + \frac{\partial}{\partial x_j}(\rho u_j Y_i) = \frac{\partial}{\partial x_j}J_{ij} + M_i \dot{w}_i$$
(10)

The diffusive flux of species *i*, $J_{i,}$ includes ordinary diffusion driven by concentration gradient and, optionally, thermally induced diffusion driven by temperature gradients. The mass diffusivities of individual species do not have to be equal with this chemistry model. The reaction rate constant to calculate the reaction rate is represented in the modified Arrhenius form:

$$k = A \cdot T^n \exp(-E/RT)$$
(11)

where *A* is the pre-exponential factor, *E* is the activation barrier, *R* is the universal gas constant and *n* is the temperature exponent. These parameters were calibrated for the current application.

4.3   Mechanisms

It is probable that reaction between Jeffamine with RDX and TNT is a multi-step process. The initiation reaction occurs probably via a highly exothermic reaction, and the energy released from the reaction is used for initiating other reactions. Probably, RDX and TNT undergo kinetically favored reactions with low activation barriers as well as with low reaction energy. Perhaps, this prevents the reactions with higher activation barrier and higher reaction energies to occur which causes explosion.

Although the actual process is expected to be a multi-step, a one step reaction of the form

Comp B + Jeffamine → Epoxy + gas
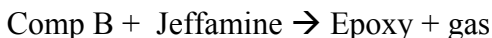
was assumed per the model to simplify the analysis.

TGA

Comment: 2.5C MIN TO 200C 59.810MG JEFF 11.997MG COMPB

E: 71.92 kJ/Mole
Log Z: 8.738 1/min
60 min half-life: 78.77°C
Conversion: 50.0 %

0.0900 hr
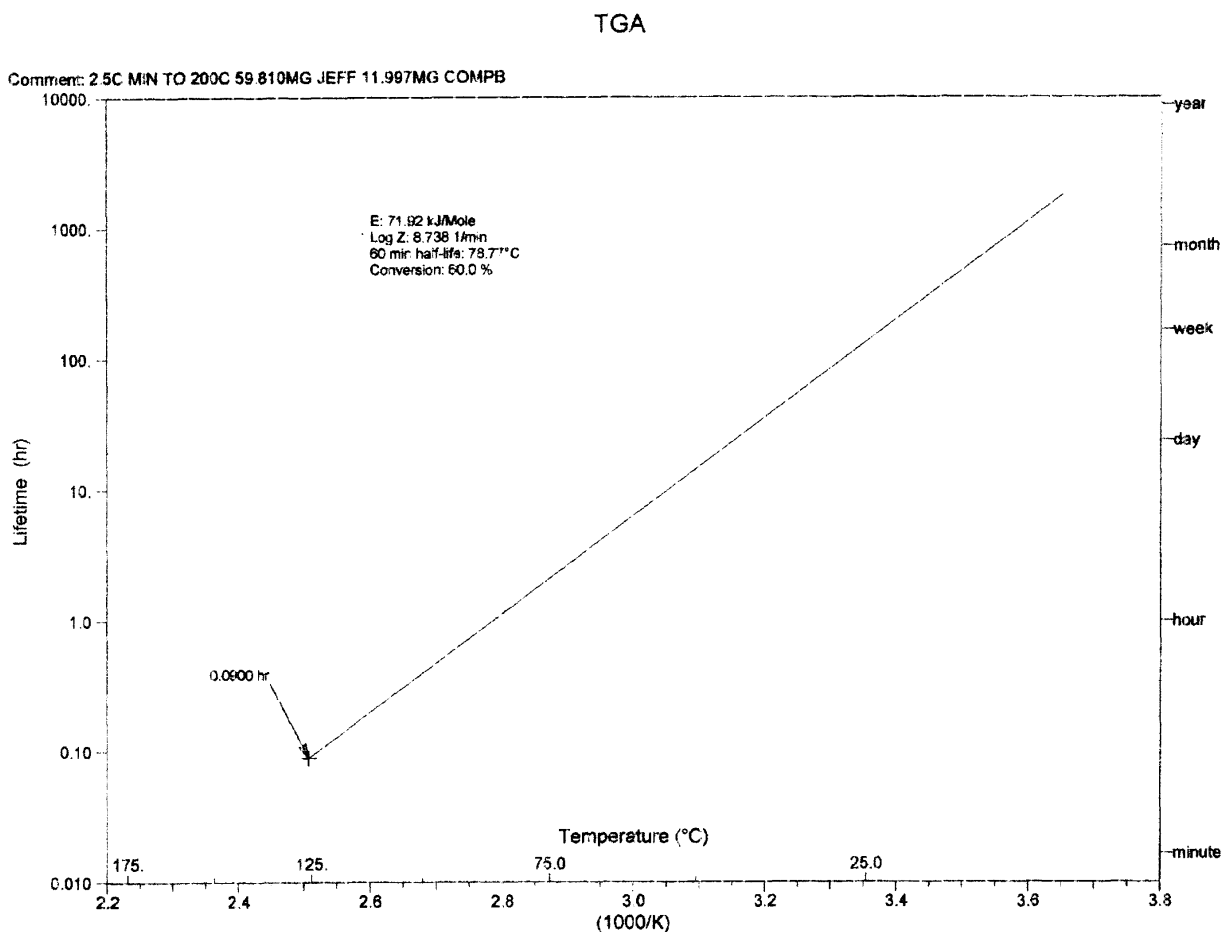
Figure 5. Conversion of Comp. B as a Function of Temperature

Figure 5 shows the temperature dependence of lifetime of Comp.B-Jeffamine mixture based on experiments conducted at Sandia National Labs. The pre-exponential factor and activation barrier have been calculated from the above plot, and their values are $9.1.10^6$ sec^{-1} (with n=0) and 17 kcal/mol, respectively. However, the numerical simulation with the above rate constant was unable to reproduce the experimental temperature profile shown in Figure 4.   This rate constant is too large to reproduce the slow temperature increase observed in experiment.   The reaction rate for the above was therefore recalibrated against the empirical data shown in Figure 4. We have chosen Arrhenius type of first order rate constant expression with pre-exponential factor and activation barrier as 5.10^{-2} sec^{-1} (with n=0) and 2 kcal/mol respectively which are much lower than the experimental value. As will be seen later, that this rate constant is able to reproduce the correct temperature *vs*. time profile. The heat of the reaction is taken from the data provided by Sandia. This value is 468 cal/gm for Comp. B and Jeffamine reaction.

In the single fluid model, there is no mechanism for the gas to escape from the liquid. In order to model the foaming, we artificially remove the gas by introducing a psuedo reaction which partially converts gas back into a liquid. Negligible energy is involved with this contrived conversion of gas back to liquid, such that it does not affect the reaction rate or the temperature. If we did not remove this gas, the simulation would predict excessive foaming to the extent that the solution would foam out of the beaker, resulting in an unrealistic mass loss.

The rate constants of the gas → liquid reaction dictates the degree of foaming. The rate constant for this reaction has been calibrated to match the foaming observed in the experiment. The pre-exponential factor for this reaction is chosen to be 0.1 sec^{-1} (n=0) with zero activation barrier. This essentially means the gas → liquid conversion is temperature independent.

4.4   Properties

Selected properties of Jeffamine and Comp B are provided in Table 2. A more complete list of properties is provided in Appendix A. The reference enthalpy of the TNT and Epoxy in the model is adjusted to correspond to the heat of reaction as measured by Sandia.

Table 2. Material Properties (Courtesy of Sandia National Laboratories)

Material	Density gm/cc	Viscosity (cps)	Density gm/cc	Conductivity Cal/sec/cm/^{o}C
Jeffamine	0.981	70 at 25C	0.981	$4.70.10^{-4}$
Compound B	1.65	11200 at 25C* 25 at 130C*	1.65	$7.68.10^{-4}$

*viscosity for mixture of Comp. B and Jeffamine

Special user-subroutines were created to compute the average density and conductivity of the fluid mixture as a function of the individual properties of the reactants and products, listed in Table 2. The formulas used are as follows:

Density:

$$\rho = \frac{1}{\sum Y_i / \rho_i}$$

where Y_i and ρ_i are the mass fraction and density of the ith species in the mixture.

Conductivity:

$$k = \sum k_i Y_i$$

where k_i are the thermal conductivities of the ith specie in the mixture.

Since the density of the fluid is a function of the gas volume, production of gas due to reaction significantly reduces the average fluid density, causing foaming and buoyancy driven flow. This foaming action reduces the effective conductivity of the fluid, increasing the potential for overheating of the reaction. The inclusion of mixture properties in the model enables the use of the code to analyze these physical effects.

4.4   <u>Model Assumptions</u>

The current model has the following Assumptions:

- ❑   Single Fluid
- ❑   Simplified One-step Mechanism
- ❑   Calibrated Rates
- ❑   Pre-melted explosives

The limitation of the single fluid approach is that it cannot model the rise of bubbles through the liquid. Instead, it considers the combination of liquid and gas as foam with common velocities. The simplified one-step mechanism treats the reaction as an averaged process, when in fact, multiple reactions are occurring. Given the assumed one-step reaction mechanism, the rates of the reaction were calibrated using empirical data.

Another assumption used in the model is that the explosives have already melted prior to the onset of reactions. Clearly, this is not the case for some of the chunk experiments. However, it does represent a "worst-case" scenario, and considering that the melting temperature of Comp B is 80C, is most likely a good assumption for the powder and flake experiments.

It is recommended that these assumptions be improved upon. However, they do not invalidate the conclusion of this report.

5.   WORK ACCOMPLISHED

The original tasks, as listed in the proposal are

- ❑   Link the CFD-ACE+ Two Fluid/Chemistry Modules
- ❑   Conduct Literature Search of Jeffamine -RDX /TNT Mechanisms
- ❑   Create a Model of the Sandia Test and Prototype Reactors
- ❑   Validate with Sandia experimental measurements
- ❑   Documentation

All of these tasks were completed, as planned, with the exception that task one was modified such that a single fluid model was adapted to model the chemical reaction and fluid dynamics of the process. The work accomplished under these tasks is described in detail below.

5.1   <u>Adapt the CFD-ACE+ Single Fluid/Chemistry Modules</u>

The Chemistry module in CFD-ACE was adapted to simulate multi-step chemistry, including the formation of a gas phase in the liquid. In this simulation, single-phase

model with chemistry has been used. Within this framework, liquid is assumed to be a incompressible gas, but the properties of the liquid have been used (such as density, thermal conductivity, molecular weight). Two user subroutines have been written in order to perform this task. They are provided in the Appendix B.

5.2   Conduct Literature Search of Jeffamine -RDX /TNT Mechanisms

No literature data were found for the reaction mechanism between RDX/TNT with Jeffamine. This includes the order of reaction, reaction rate constants of every reaction pathways as a function of temperature. We therefore decided to calibrate the rate constant assuming that the entire process happens in one step. We preferred to use one-step reaction mechanism as opposed to multi-step. Number of unknown parameters in the multi-step mechanism would be large, and is therefore difficult to calibrate. In the one-step mechanism there are two unknown parameters (pre-exponential factor and the activation barrier) to be calibrated, and therefore relatively easier.

5.3   Create a Model of the Sandia Test and Prototype Reactors

Two-dimensional models of both the laboratory beaker experiment and the full scale reactor (four times the size of the laboratory beaker) were created. Figure 6 shows the model of the beaker reactor, with sample initial conditions and boundary conditions. The boundary conditions were set up to mimic the experiments as shown in Figure 4. For example, the boundary condition of the bottom wall of the beaker was set to the measured temperature profile of the hot plate heater element. The initial temperature of the mixture solution was set to 353K, which was the Jeffamine temperature when the Comp B was added.

Figure with labels: "outlet", "N$_2$ at 300K", "Newton cooling dq/dt = h(T$_w$-T$_{inf}$)", "Radiation : $\varepsilon\sigma(T_w^4 - T_{inf}^4)$", "15.24 cm", "CompB+Jeffamine 353K", "2.54 cm", "Time dependent heating", "7.62 cm"
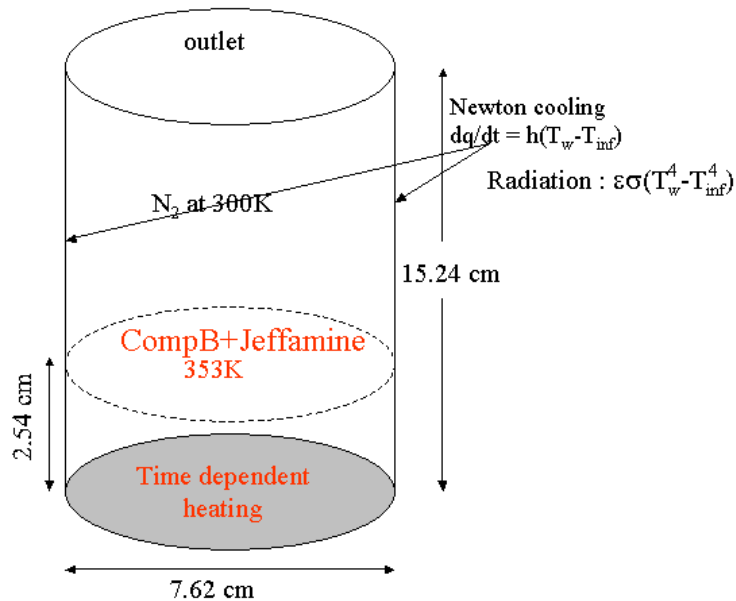
Figure 6.   Numerical Model of the Beaker Experiment. The temperature of the bottom of the beaker is set according to the heating rate provided in Figure 4. External heat transfer and radiation boundary condition are applied to the sidewall of the beaker.

5.4   Validate with Sandia Experimental Measurements

The model was calibrated using the data in Figure 4. As discussed in Section 4.3. This required adjusting the pre-exponential and activation barrier of the assumed one step reaction. The numerical simulation was started at an experiment elapsed time of 270 seconds, which corresponds to the addition of Comp B powder.

Figure 7 provides a comparison of the predicted versus measured temperatures of the hot Jeffamine solution.

Sandia Energetic Materials Neutralization
Jeffamine + Comp B Explosive Powder
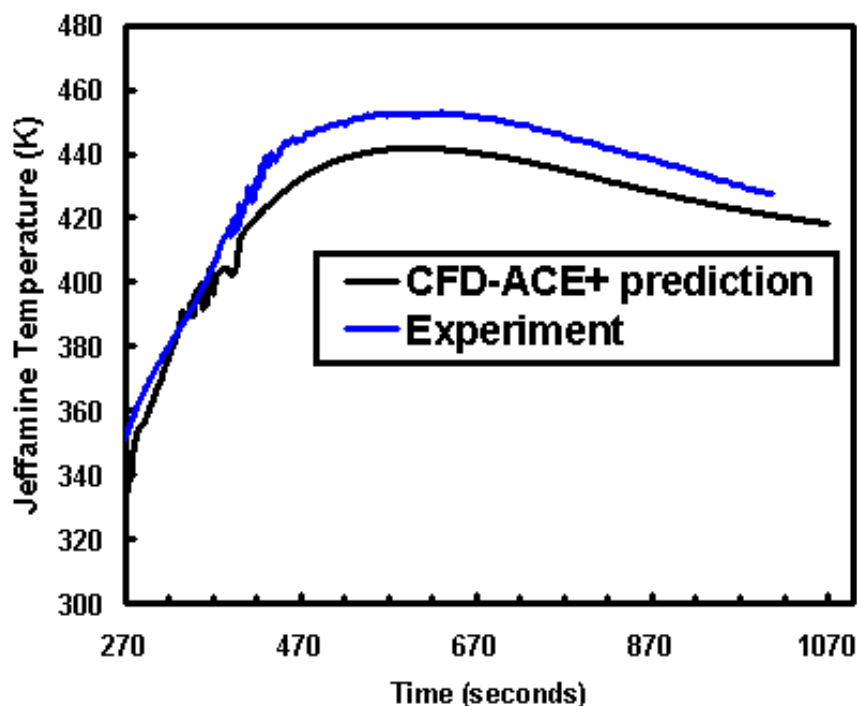**(Test Date: 22 Feb 2001)**

Figure 7. Comparison of Experimental Temperature Profile with the Simulation

Qualitatively the simulated temperature profile matches quite well with the experiment. This correlation includes the oscillations observed in both the experiment and the model during the rapid heat-up from approximately 320 to 420 seconds. These fluctuations are due to gravity driven convective rolls in the beaker. The model also matches the cool down phase of the solution quite well.

Quantitatively, the match between the experiment and the prediction is also reasonable, with the model predicting time of maximum temperature very well and the maximum temperature to within 10 degrees.

5.5   **Parametrics**

The calibrated model was used to investigate the effect of initial mixing, scale-up, and mixture ratio on the maximum temperature in during reaction.

Pre-mixing:
One concern is that the extent of melting and mixing, prior to the initiation of reaction, is expected to have a significant effect on the reaction rate. For example, large chunks, which would be expected to melt more slowly, would most likely begin reacting prior to fully melting. The existence of solid chunks would delay mixing of the explosive with the Jeffamine, and reduce both the reaction rate and the maximum temperature. On the contrary, thin flakes, which would more easily melt and mix, might result in rapid reaction and explosive temperatures. It is possible to investigate this effect in the model

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by starting with different initial degrees of mixing. For the baseline, the Comp B and the Jeffamine were assumed to be fully melted and fully mixed. As a comparison, a subsequent simulation was conducted, using the same proportions of Comp B and Jeffamine, but with the Comp B initially concentrated in a melted "blob" in the middle of the beaker.

The predicted temperature for of the unmixed case is very similar to the fully mixed case, as shown in Figure 8. This is because, at the relatively slow reaction rates in the baseline case (on the order of minutes), there is sufficient time for the explosive and Jeffamine to fully mix due to natural convection. For a faster reaction, this might not be the case.
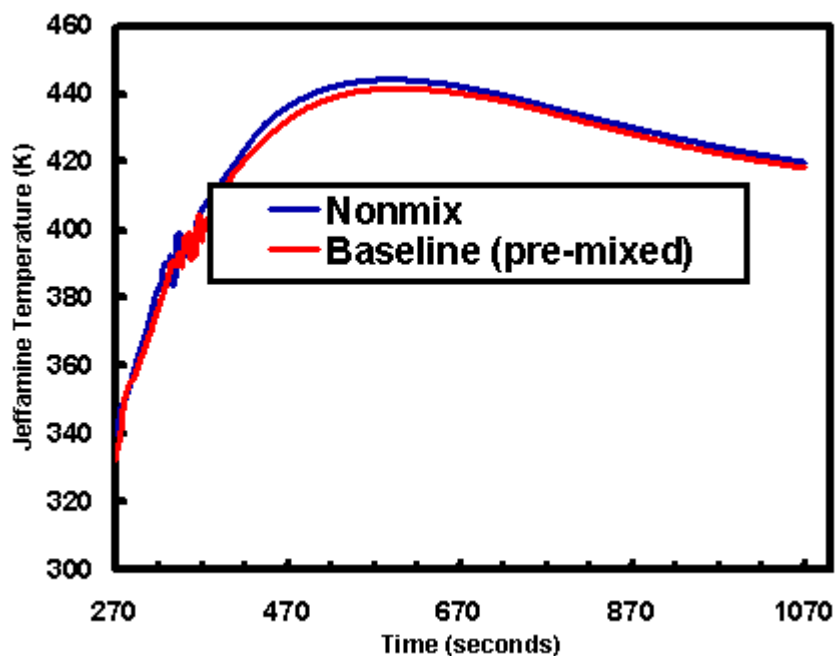
Figure 8.   *Temperature Profile of Baseline Case (pre-mixed) vs. Non-Mixed Case. The maximum temperature for the mixed case is slightly higher than that of non-mixed case*

Scale-up:

The concern with scale-up is that as the reactor gets bigger, the volume of reactants gets larger by a factor of the characteristic length cubed, while the surface area available to cool the reaction only increases as a function of the square of this length. As such, hotter temperatures are expected for larger reactors, with the same relative proportion of reactants. In order to investigate this effect, a large-scale model was created. This model is 4 times larger than the laboratory scale beaker and resembles the actual full scale reactor used by Sandia (Figure 9). The model was then run using the same ratio of Comp. B to Jeffamine, as for the beaker scale reactor. The result is that the maximum temperature increases by nearly 69 degrees and occurs later in the process, as shown in Figure 10.
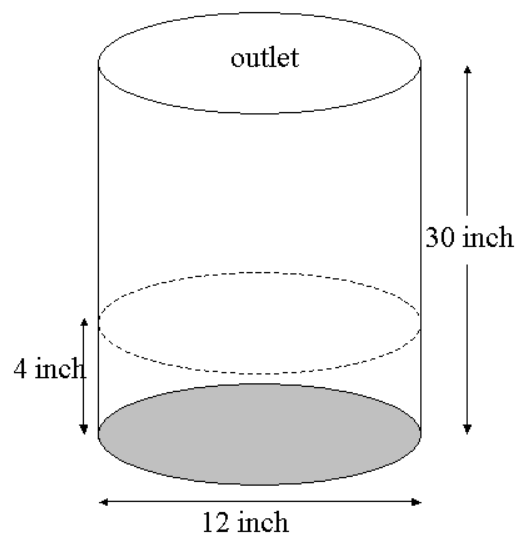
Figure 9. Geometry of the Actual Full Scale Reactor
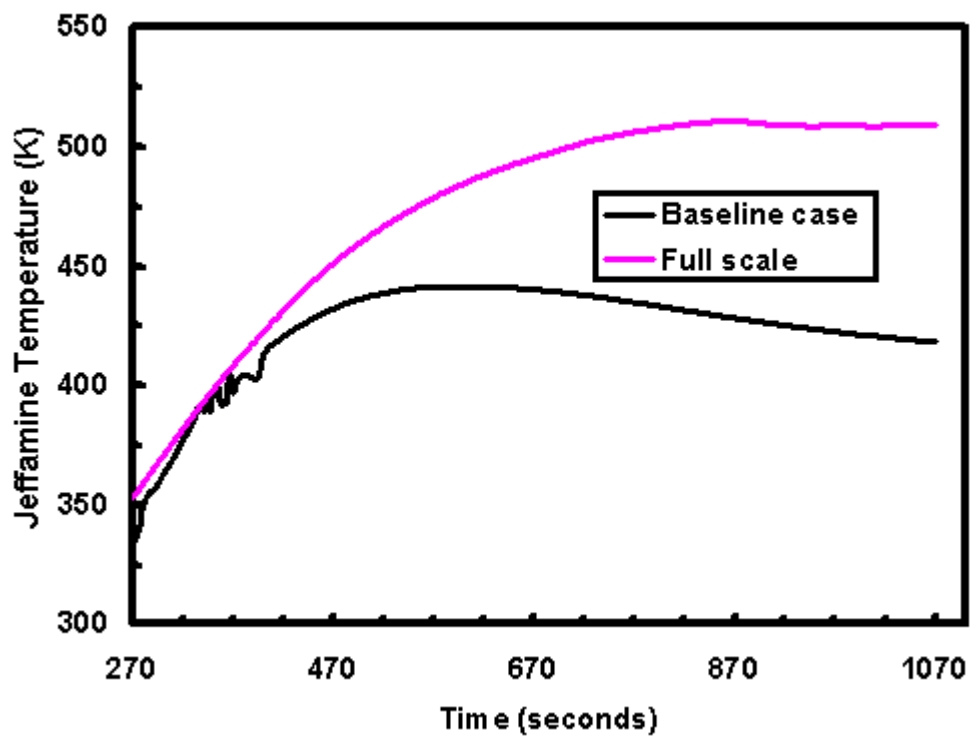
*Figure 10.   Comparison of Temperature Profile for the Baseline Case and to the Full
Scale Reactor*

Mixture ratio:

During reaction, the Jeffamine acts as a heat sink. In the experiments to date, the reaction was conducted using an excess of Jeffamine. If, instead, only the amount of Jeffamine required to react with the Comp B were used, the maximum temperature would be higher. This case was investigated by repeating the baseline case with 58 grams of Jeffamine instead of 97gms. The result was an increase in the peak temperature (see Fig. 11). These results indicate that Jeffamine is acting as a heat sink. Also, the maximum temperature is reached relatively quicker when less Jeffamine is used.
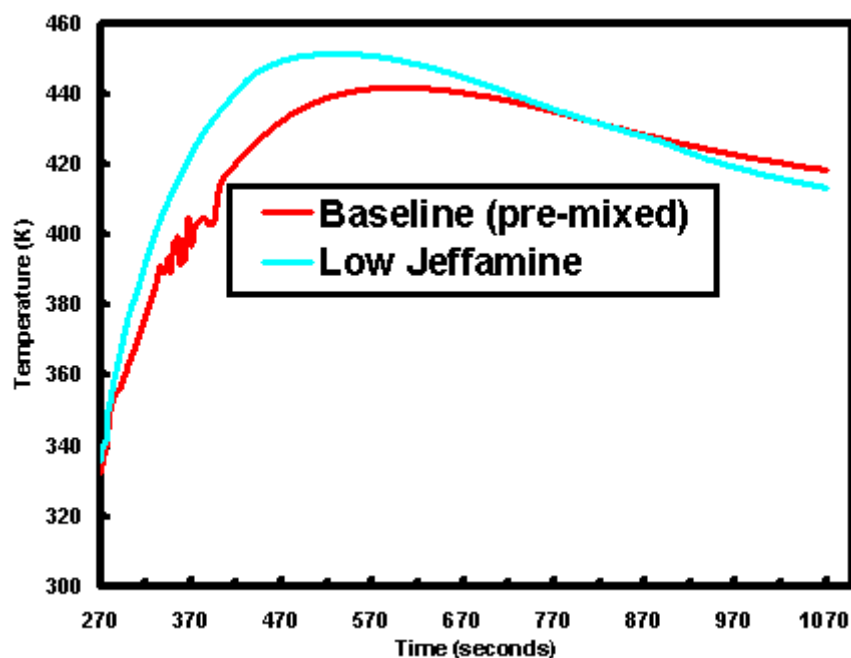
Figure 11.   Effect of Maximum Temperature on the Amount of Jeffamine.   Value of maximum temperature increases when less Jeffamine is used.

In summary of parametric studies, Table 3 shows the relative increase or decrease in the maximum monitoring point temperature relative to the baseline case.

Table 3. Parametric Study

	Time to Max T	Max T	Delta T
Baseline	**~597 sec**	**442K**	**0**
Unmixed	**~592 sec**	**444K**	**2K**
Decreased Jeffamine	**~532 sec**	**451K**	**9K**
Full Scale	**~868 sec**	**511K**	**69K**

Figures 12 and 13 provide two-dimensional images of the predicted reaction process. The images are split in half to present density on the left side and temperature on the right. Figure 12 shows the initial condition for the simulation (this corresponded to 270 elapsed time in the experiment). Figure 13 shows subsequent predicted temperature and density profiles at different stages of the reaction. The monitor points are indicated by the cross signs "+." These monitor points correspond to the position of the thermocouple in the laboratory experiments. During the early stage of the reaction (approximately 370-470 seconds) there is a strong re-circulation near the bottom thermocouple. This buoyancy driven convection gives rise to the local oscillations in the measured Jeffamine temperatures evident in both the experimental data and the numerical predictions (Figures 7,8,10 and 11). Figure 13 shows the density change (or foaming) as a function of time. Based on the velocity field, the model predicts that the foam has begun to recede starting at approximately 414 seconds, even before the reaction temperature has peaked (597 seconds). Experimentally, this change in foam level is indicated by the thermal response of the upper thermocouples at the 425 and 600 ml level (figure 4). Note that the top thermal couple appears to be uncovered at 7 minutes (420 sec). Thus the predicted onset of the foam recession is very close to that indicated by the experimental data. Figure 14 provides a plot of the predicted temperature as "measured" at the numerical monitoring point corresponding to the 425 ml thermocouple. Although the thermal response at this monitoring point is temporally smeared due to the inaccuracy of the single fluid model in modeling foam formation and collapse, it indicates a qualitative rise in temperature similar to that of the real data.

One last important observation is that the position of the maximum temperature in the beaker is predicted to occur near the middle of the solution (see Figure 13 at 600 sec). This indicates that reaction is still occurring in the foam near the top of the beaker, with a corresponding temperature build-up. Furthermore, it indicates that a single thermocouple (e.g. such as the bottom thermocouple in the baseline case) located at the periphery may provide a misleading peak temperature which is significantly lower than the real peak.

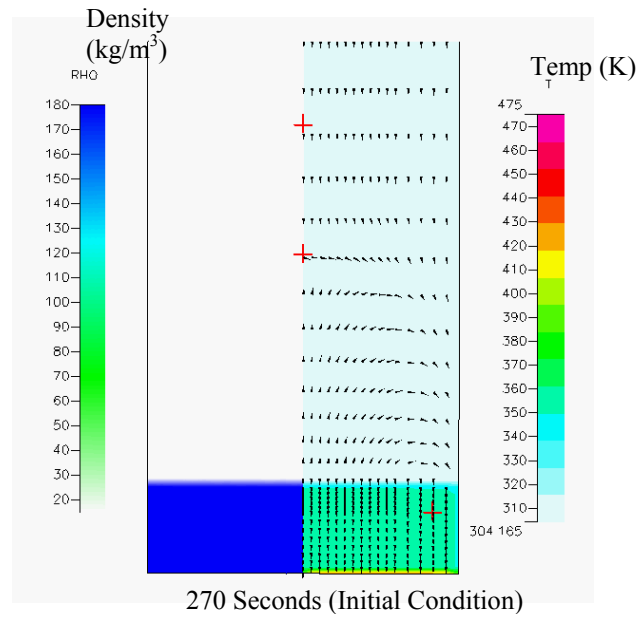*Figure 12.   Initial Conditions for the Simulation. Density and temperature are expressed in kg/m³ and Kelvin.*

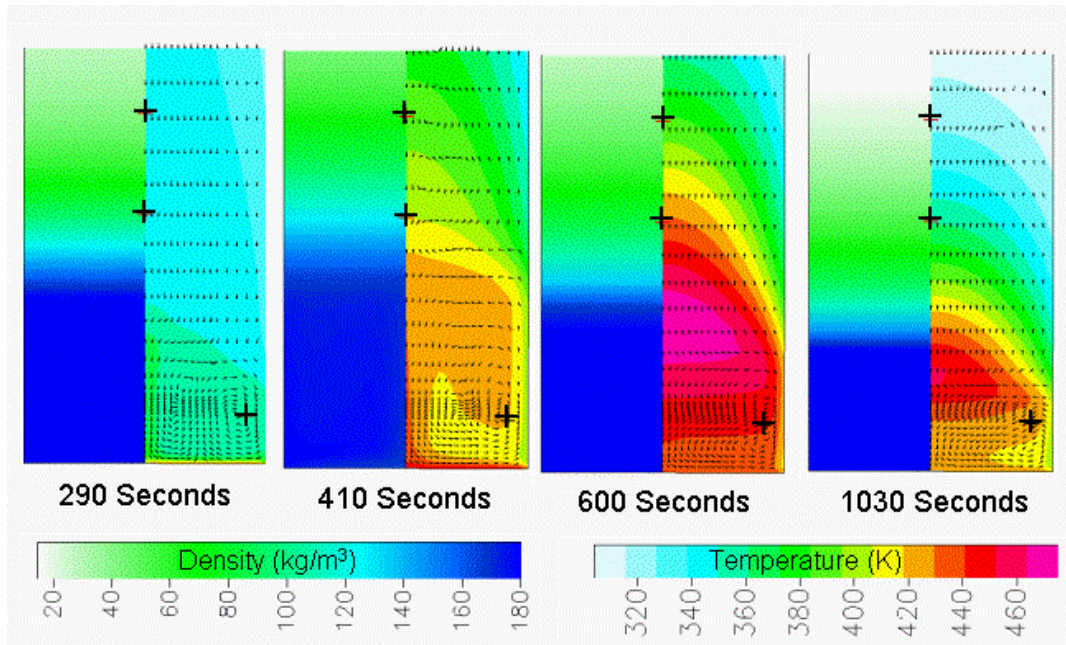*Figure 13.   Temperature and Density Profile at Different Stages of the Reaction. Temperature and density are expressed in Kelvin and kg/m³, respectively. The "+"signs indicate the positions of the thermocouples.*

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Predicted Temperature at Two Thermocouple Locations
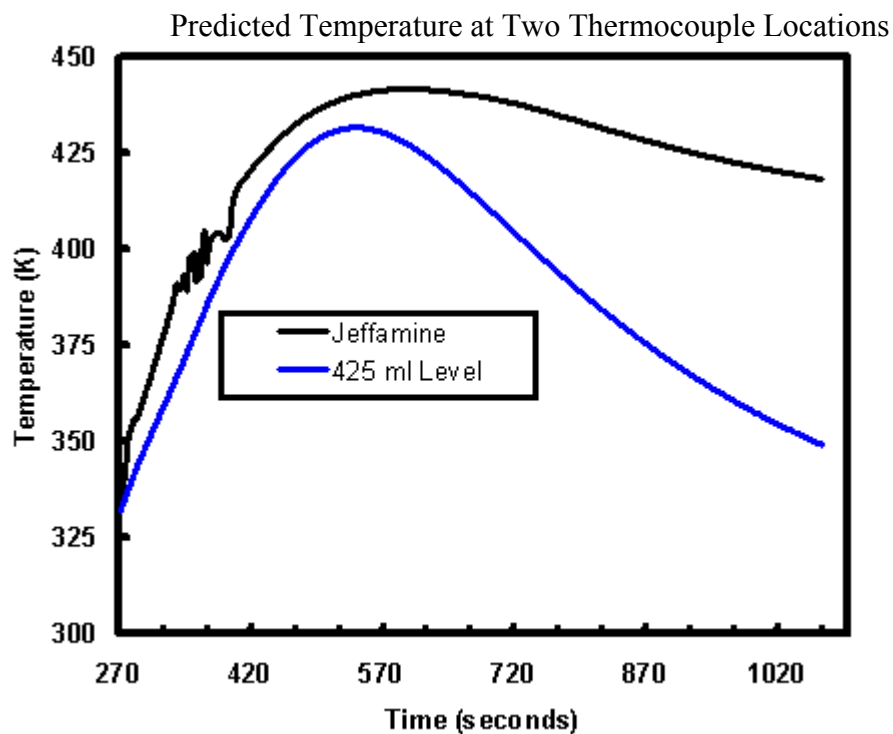
Figure 14.   Temperature Profile at the 425 ml Llevel of the Beaker Compared to that of Jeffamine Solution

7.   RECOMMENDATIONS AND FUTURE TASKS

Based on the above simulations, the following recommendations are made:

When scaling up, reduce the proportion of explosive to Jeffamine such that the increase in the quantity of explosive mass is directly proportional to the increase in surface area of the container.

Since Jeffamine acts as heat sink, a low proportion of Jeffamine may increase the temperature of the reaction. A higher proportion of Jeffamine is therefore recommended.

For a slow process (e.g. on the order of minutes), pre-mixing of the explosive and Jeffamine is not predicted to make much difference in the maximum temperature, since natural convection has time to mix the reactants during the reaction process. However, whether the materials are pre-mixed or not would be expected to influence the reaction time and the corresponding peak temperature for faster reaction times.

The hottest temperatures are predicted to occur in the center of the solution. Consequently, care should be exercised when adding addition reactants to the top of the reactor. Fresh material will be in contact with fluid at much higher temperatures than indicated by a thermocouple positioned near the bottom of the tank. Also, the mixer should be designed to reduce thermal stratification and the thermocouple(s) positioned to record the true maximum.

We expect the reaction occurring within the beaker is a complex, multi-step process as opposed to the simple one-step reaction assumed in the model. In order to perform simulation with experimental rate constant, the rate constants measurements of all steps should be performed. In addition, a two fluid model with chemistry would be required to more accurately predict the foaming action associated with this process.

APPENDIX A: Properties

Temperature Variation of Viscosity

Viscosity Tests of Liquid By-Products

Sandia Nat/l Labs								12/8/2000
Jeffamine + high explosives reactions								P. Walker

PROPERTIES OF REACTANTS AND PRODUCTS:

	Density (g/cm^3)	Melt pt. (C)	Heat of reaction (calories/gram of explosive)	Spec. heat (cal/g-°C)	Thermal conduct. (cal/sec/cm/°C)	Viscosity at 25 C (cps)	Viscosity at 130 C (cps)
Reactants:							
TNT solid	1.59	81		at 80C=0.374	8.83E-04	n/a	n/a
TNT liquid	1.47						
RDX solid	1.82	204		at 140C=0.446	6.91E-04	n/a	n/a
Comp B solid	1.65	78-80		at 100C=0.312	7.68E-04	n/a	n/a
(60%RDX+40%TNT)							
Jeffamine	0.981	n/a		at 130C=2.03	4.70E-04	70	
					approx.		
Products :							
TNT + jeff		n/a				12,816	34
(10% by wt)							
RDX + jeff	1.03	n/a				6756	24
(25% by wt)							
Comp B + jeff		n/a	468			11,200	25
(20% by wt)							
Jeffamine							

Temp C	Heat capacity J/g/deg C
50	1.583
60	1.626
70	1.674
80	1.724
90	1.782
100	1.848
110	1.880
120	1.988
130	2.030
140	2.039
150	2.011
160	1.962
170	1.924
180	1.878
190	1.814

User Subroutines
```
!*********************************************************************
 MODULE cfdrc_user
!*********************************************************************
  IMPLICIT NONE

  INTEGER, PARAMETER :: int_p  = SELECTED_INT_KIND(8)

  INTEGER, PARAMETER :: string_length = 80

  INTEGER, PARAMETER :: real_p = SELECTED_REAL_KIND(8)

  INTEGER, PARAMETER :: XDIR = 1, YDIR = 2, ZDIR = 3

! Utility parameters.
  REAL(real_p) , PARAMETER :: zero = 0.0d0, one = 1.0d0, two = 2.0d0,   &
                  three = 3.d0, four = 4.0d0,            &
                  pi = 3.1415926535898d0

  LOGICAL:: first_time = .TRUE., error,first_time1 = .TRUE.

  INTEGER(int_p) :: ind_SANNO2=0, ind_TNT=0, ind_TNTB=0,     &
              ind_N2=0, ind_JEFF=0,ind_VOL=0,ncells=0,ind_DENS=0

  REAL(real_p) :: sum_first=0.0
! Declare global variables
! USER CODE BEGIN


! USER CODE END

 END MODULE cfdrc_user

SUBROUTINE ucond(iopt, vcindex)
!*********************************************************************
! copyright (c) 1998  cfd research corp.  all rights reserved.
!
! purpose : set local conductivity
!
! iopt:  option for ways of specifying conductivity
!
! This routine is called on a cell-by-cell basis for each user-defined
! conductivity for each zone or volume condition where conductivity is
```

```fortran
! specified as user defined.
!
! Use get_active_cell_index(ic,error) to get the current cell index in
! the volume condition.
!
! One may use get_value_one_cell to obtain values of various dependent
! variables such as temperature, velocity etc.
!
! Use set_value_one_cell to set the value for conductivity.
!
!-------------------------------------------------------------------

! Include required global variables declared in cfdrc_user module.
  USE cfdrc_user


  IMPLICIT NONE
  REAL(real_p) , PARAMETER :: cond_SANNO2=0.0236,cond_TNT=0.37d0,    &
                cond_JEFF=0.1974d0, cond_N2=0.0236,          &
                cond_TNTB=0.1974d0
  INTEGER(int_p), INTENT(IN) :: iopt, vcindex


  REAL(real_p) :: SANNO2_mass_f, TNT_mass_f, TNTB_mass_f,N2_mass_f,  &
          cond_cell, JEFF_mass_f
  INTEGER(int_p) ::      ind_COND

  CHARACTER(len = string_length) :: var_name

  INTEGER(int_p) :: ic

! Declare required local variables here.
! USER CODE BEGIN


! USER CODE END

!-------------------------------------------------------------------

!el@uiuc.edu Start writing code here.
! USER CODE BEGIN

  IF (first_time) THEN

   first_time = .FALSE.
   CALL get_cells(ncells,error)
```

```
var_name = 'SANNO2'
CALL get_var_index(var_name, ind_SANNO2, error)


var_name = 'TNTB'
CALL get_var_index(var_name, ind_TNTB, error)

var_name = 'TNT'
CALL get_var_index(var_name, ind_TNT, error)

var_name = 'JEFF'
CALL get_var_index(var_name, ind_JEFF, error)

var_name = 'N2'
CALL get_var_index(var_name, ind_N2, error)

var_name = 'THERMAL_CONDUCTIVITY'
CALL get_var_index(var_name, ind_COND, error)

var_name = 'VOLUME'
CALL get_var_index(var_name, ind_VOL, error)

ENDIF

CALL get_active_cell_index(ic,error)

CALL get_value_one_cell (ind_SANNO2, ic, SANNO2_mass_f, error)


CALL get_value_one_cell (ind_TNT, ic, TNT_mass_f, error)

CALL get_value_one_cell (ind_JEFF, ic, JEFF_mass_f, error)

CALL get_value_one_cell (ind_TNTB, ic, TNTB_mass_f, error)


CALL get_value_one_cell (ind_N2, ic, N2_mass_f, error)

cond_cell = SANNO2_mass_f * cond_SANNO2 + TNT_mass_f*cond_TNT  &
     + TNTB_mass_f * cond_TNTB + N2_mass_f*cond_N2             &
     +JEFF_mass_f*cond_JEFF

CALL set_value_one_cell (ind_COND, ic, cond_cell, error)
```

```fortran
! USER CODE END

  RETURN
 END SUBROUTINE ucond

SUBROUTINE udens(iopt, vcindex)
!********************************************************************
! copyright (c) 1998  cfd research corp.  all rights reserved.
!
! purpose : set local density
!
! iopt:  option for ways of specifying density
!
! This routine is called on a cell-by-cell basis for each user-defined
! density for each zone or volume condition where density is specified
! as user defined.
!
! Use get_active_cell_index(ic,error) to get the current cell index in
! the volume condition.
!
! One may use get_value_one_cell to obtain values of various dependent
! variables such as temperature, velocity etc.
!
! Use set_value_one_cell to set the value for density.
!------------------------------------------------------------------

! Include required global variables declared in cfdrc_user module.
  USE cfdrc_user

  IMPLICIT NONE


! Declare required local variables here.
! USER CODE BEGIN


! USER CODE END

!  REAL(real_p) :: den_TNT,den_JEFF, &
!                  den_TNTB
  REAL(real_p) , PARAMETER :: den_TNT=1650.0d0,den_JEFF=981.0d0, &
                  den_TNTB=981.0d0
  INTEGER(int_p), INTENT(IN) :: iopt, vcindex


  REAL(real_p) :: SANNO2_mass_f, TNT_mass_f, TNTB_mass_f,N2_mass_f,  &
```

```fortran
            den_cell, JEFF_mass_f,den_SANNO2,den_N2,wt_SANNO2, &
            wt_N2,cell_T

INTEGER(int_p) ::  ind_T
CHARACTER(len = string_length) :: var_name

INTEGER(int_p) :: ic

IF (first_time1) THEN

 first_time1 = .FALSE.

 var_name = 'SANNO2'
 CALL get_var_index(var_name, ind_SANNO2, error)

 CALL get_species_mol_wt(ind_SANNO2,wt_SANNO2,error)

 var_name = 'TNTB'
 CALL get_var_index(var_name, ind_TNTB, error)

 var_name = 'TNT'
 CALL get_var_index(var_name, ind_TNT, error)

 var_name = 'JEFF'
 CALL get_var_index(var_name, ind_JEFF, error)
 var_name = 'N2'
 CALL get_var_index(var_name, ind_N2, error)

 CALL get_species_mol_wt(ind_N2,wt_N2,error)

 var_name = 'DENSITY'
 CALL get_var_index(var_name, ind_DENS, error)

 var_name = 'T'
 call get_var_index(var_name,ind_T,error)

ENDIF

CALL get_active_cell_index(ic,error)

CALL get_value_one_cell (ind_SANNO2, ic, SANNO2_mass_f, error)

CALL get_value_one_cell (ind_TNT, ic, TNT_mass_f, error)

CALL get_value_one_cell (ind_JEFF, ic, JEFF_mass_f, error)
```

```fortran
      CALL get_value_one_cell (ind_TNTB, ic, TNTB_mass_f, error)


      CALL get_value_one_cell (ind_N2, ic, N2_mass_f, error)

      CALL get_value_one_cell (ind_T,ic,cell_T,error)

       den_SANNO2 = 101300.0d0 * wt_SANNO2/(8314.0d0*cell_T)
       den_N2 = 101300.0d0 * wt_N2/(8314.0d0*cell_T)

      den_cell = SANNO2_mass_f/den_SANNO2 + TNT_mass_f/den_TNT   &
            + TNTB_mass_f/den_TNTB + N2_mass_f/den_N2               &
            +JEFF_mass_f/den_JEFF
      den_cell = 1.0d0/den_cell

      CALL set_value_one_cell (ind_DENS, ic, den_cell, error)


       RETURN
      END SUBROUTINE udens

SUBROUTINE uout(iflag)
!*********************************************************************
! copyright (c) 1998  cfd research corp.  all rights reserved.
!
! purpose : for customized user output.
!
! iflag:  flag indicating calling location.
!
! This routine is called 5 times at different instances of iterative
! cycle indicated by iflag.
!
! iflag  :
!       0 - At the beginning (only for dtf reading calls, At this point
!                   most of the other data may not be available.
!                   users can get variable indices, and may be
!                   external reading of files can be done with this
!                   flag = 0)
!       1 - At the beginning of RUN. (At this poin most of the boundary
!                       conditions, properties are set. users
!                       should be able to get cell or boundary
!                       values for different variables.)
!       2 - At the beginning of time step (only for transient problems).
!       3 - At the end of each iteration.
!       4 - At the end of each time step.(only for transient problems).
!       5 - At the end of RUN.
```

```fortran
!
! One may use get_value_one_cell to get the values. To get the cell
! indexes, user has to supply the x,y,z locations and use the
! get_cell_index(vc_index,x,y,z,ic_global,error).
!---------------------------------------------------------------------

! Include required global variables declared in cfdrc_user module.
  USE cfdrc_user

  IMPLICIT NONE

  REAL(real_p) :: VOL,sum,den_cell,TNT_mass_f,timet,ratio,sum_vol,sum1
  INTEGER(int_p), INTENT(IN) :: iflag
  INTEGER(int_p) :: i,user_iflag,time_step_no


!---------------------------------------------------------------------


   user_iflag = 4
   if(iflag /= user_iflag) RETURN
   sum = 0.0d0
   sum1 = 0.0d0
   CALL get_time(timet,time_step_no,error)
 DO i=1,ncells
  CALL get_value_one_cell(ind_VOL,i,VOL,error)
  CALL get_value_one_cell(ind_TNT,i,TNT_mass_f,error)
  CALL get_value_one_cell(ind_DENS,i,den_cell,error)

  sum = sum+TNT_mass_f*den_cell*VOL
  sum1 = sum1 + den_cell*VOL
 ENDDO
 IF(time_step_no == 1) sum_first = sum
 ratio = sum/sum_first
 write(10,*) timet, ratio,sum1

 RETURN
END SUBROUTINE uout
```

Distribution

	MS-1452	Billy Marshall, 2552
	MS-1452	Pamela K. Walker, 2552
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1	MS-9018	Central Technical Files, 8945-1
2	MS 0899	Technical Library, 9616
1	MS 0612	Review & Approval Desk, 09612 for DOE/OSTI